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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

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basic compounds, the alkaline bicarbonates produce, immediately if they are added in excess, in the nitrate and sulphate similar red-brown precipitates as the solutions of the neutral carbonates; but in the solution of the perchloride of mercury they merely give rise to a faint whitish opacity; only after some time is a greater or less amount of a reddish-brown precipitate of a basic salt formed in proportion as the carbonic acid escapes. Carbonate of lime and baryta behave like the bicarbonates; both immediately precipitate reddish-brown precipitates from the solution of the pernitrate of mercury; but from the persulphate dissolved in sulphuric acid, mineral turpeth, which becomes brownish-red by long standing, especially when heated with carbonate of baryta. On the contrary, carbonate of lime or baryta produce no precipitate in a solution of the perchloride of mercury, or at the utmost only a slight reddish-brown tint is formed on boiling at the margin of the vessel. Perchloride of mercury is not altered, either in the cold or on boiling, by a solution of protosulphate of iron; while from the solution of the nitrate or sulphate the whole of the mercury is eliminated, even in the cold, by the protosulphate of iron. The solution of the perchloride of mercury contains consequently no muriate of the oxide which would be reduced by the protosulphate of iron. The greater affinity of the mercury for chlorine than for oxygen is moreover evident from the circumstance that nitric acid, and even sulphuric acid, do not decompose the perchloride of mercury, and convert it into an oxysalt, either with or without the application of heat. The protosalts of mercury cannot be compared with the protochloride, on account of the insolubility of the latter; but that the mercury is likewise, in this case, combined more intimately with the chlorine than in the salts with oxygen and acids, is evident from the fact that the protosulphate of iron does not decompose the moist protochloride of mercury, while the mercury is instantly precipitated in a metallic state from a solution of the protonitrate by a solution of the protosulphate of iron. On this account a solution of protochloride of iron likewise produces in protonitrate of mercury a precipitate of protochloride, which is not decomposed by any excess of the protochloride of iron. In like manner the protochloride of mercury is not decomposed by carbonate of baryta or lime, or the bicarbonates of the fixed alkalies, while these readily decompose solutions of the protonitrate of mercury.

The chloride and the oxysalts of silver exhibit a very similar behaviour. Recently precipitated moist chloride of silver is not decomposed by protosulphate of iron; while, as is well known, the whole amount of silver can be precipitated from the solution of the nitrate by that salt. When a solution of nitrate of silver is mixed with one of protochloride of iron, only chloride of silver separates, and no metallic silver. Again, solutions of the alkaline carbonates do not decompose the chloride of silver in the cold, and only to a very slight extent on the application of heat. A solution of caustic potash likewise effects a decomposition of the chloride of silver only when heated. Palladium exhibits similar properties; protosulphate of iron

produces no elimination of metallic palladium in a solution of the protochloride, but it does in the solution of the nitrate, from which the metal is eliminated after some time in the form of a bright metallic pellicle, which covers the sides of the vessel and the surface of the liquid. Carbonate of baryta does not precipitate any protoxide of palladium from a solution of the protochloride, but it does from the protonitrate even in the cold.

Similar phænomena are manifested by platinum. Carbonate of baryta does not precipitate any oxide of platinum from the solution of the chloride, while the oxide is entirely separated from solutions of the sulphate and the nitrate by long boiling with carbonate of baryta. The sulphate of platinum for these experiments was obtained by treating the chloride with sulphuric acid and evaporating to dryness; the nitrate by treating the sulphate with nitrate of baryta. Protosulphate of iron produces no change in a solution of the chloride of platinum, while sometimes a complete reduction of the platinum is effected in the solution of the protonitrate of platinum by long standing with a solution of protosulphate of iron. It is however remarkable that, as was first observed by Chenevix, a mixture of perchloride of mercury and chloride of platinum is reduced after some time by the protosulphate of iron; a solution of the pernitrate of mercury mixed with platinum is likewise reduced by the protosulphate of iron; but if a solution of the protonitrate of mercury is employed in its stead, a brown precipitate is immediately formed, which subsequently becomes black. Chenevix found that the metal was precipitated by protosulphate of iron from the protonitrate of palladium; and as a similar precipitate was obtained from chloride of platinum and perchloride of mercury, he concluded that palladium consisted of platinum and mercury, especially as in some rare cases he observed a remote resemblance with respect to the fusibility and specific gravity of the reduced metal. In these cases, as was subsequently shown by Descotils, boride of platinum, which bears some resemblance to palladium, had been formed by the addition of borax.—*Proceedings of the Berlin Academy.*

Examination of Sugar of Gelatine. *By* Prof. Mulder.

The researches of Dessaigne having shown that hippuric acid is decomposed into benzoic acid and sugar of gelatine*, the author was led to suspect that the composition of sugar of gelatine is not $C^8 H^9 N^2 O^7$, but $C^8 H^{10} N^2 O^8$. In the former experiments of the author, Marchand and Boussingault, the substance probably still contained some leucine. Sugar of gelatine, frequently recrystallized from weak alcohol and dried at 212°, gave—

Carbon	32·11	8	= 32·00
Hydrogen	6·85	10	6·67
Nitrogen	18·73	2	18·67
Oxygen	42·31	8	42·66

* Chem. Gaz., vol. iv. p. 14.

The lead salt of the sugar of gelatine is difficult to obtain pure, and did not afford satisfactory results, as the amount of water was always too low, while that of the lead was too high:—

Carbon	..	13·41	13·57	8 =	13·53
Hydrogen	2·06	2·19	2·13	8	2·25
Nitrogen.....	..	..	..	2	7·88
Oxygen	..	..	..	6	13·52
Oxide of lead ..	64·93	..	..	2	62·86

On that account a salt of copper was prepared by digesting sugar of gelatine with oxide of copper and water, and evaporating to crystallization. The salt, dried at 212°, gave—

Carbon.....	22·87	8 =	22·73
Hydrogen.....	3·86	8	3·79
Nitrogen	..	2	13·26
Oxygen	..	6	22·72
Oxide of copper	37·14	2	37·50

The combination of sugar of gelatine with nitric acid possesses, in the anhydrous state in the salts with excess of base, the composition $C^8 H^5 N^2 O^6 + 2NO^5$. In the hydrated state it contains 4 equivs. HO. A salt of lead, dried at 266°, gave 45·92 per cent. oxide of lead. The composition of the lead salt was

$$C^8 H^3 N^2 O^6 + 2NO^5 + PbO + 2HO.$$

A persalt of copper gave the formula

$$C^8 H^3 N^2 O^6 + 2NO^5 + 3CuO + HO,$$

a proof that the formula for the acid must not be halved. A salt of baryta led to the formula

$$C^8 H^3 N^2 O^6 + 2NO^5 + 3BaO.$$

The author found for the composition of the free acid dried over sulphuric acid—

Carbon	18·13	8	=	17·40
Hydrogen	4·31	12		4·29
Nitrogen.....	..	4		20·30
Oxygen	..	20		58·01

Journ. für Prakt. Chem., xxxviii. p. 294.

On the Occurrence of Mannite in the Roots of Triticum repens. *By* A. Völcker.

As is well known, Pfaff discovered a kind of sugar in the roots of the couch grass, which Berzelius is inclined to regard as mannite. Some time ago Dr. Stenhouse* repeated the experiments with various quantities of couch grass, but without obtaining any mannite; and showed that the acicular crystals which he procured from the alcoholic solution were not sweet, and on closer examination they were found to consist of binoxalate of potash. It is

* Chem. Gaz., vol. ii. p. 375.

however certain that mannite occurs in the roots of the couch grass; I have frequently had occasion to observe it. The greatest quantity I have found in an extract which had been prepared from roots grown in the hot and dry summer of 1832. The perfectly clear extract solidified after a time almost entirely to a crystalline mass consisting of minute needles. They dissolved in boiling alcohol, and separated again on cooling. By frequent recrystallization, and boiling with animal charcoal, perfectly pure, long colourless prisms of silky lustre were obtained, which presented all the properties of mannite. On analysis they gave—

Carbon.....	39·48	39·59	8 =	39·71
Hydrogen ..	7·71	7·59	9	7·42
Oxygen	52·81	52·82	8	52·87

It is certain therefore that the sweet crystals from *Triticum repens* are mannite. I will not however venture to assert that mannite can be obtained from all couch grass, for the temperature seems to exert great influence on the quantity of mannite contained in the roots. I have always found that the extract prepared from roots which had been collected in dry localities and hot seasons was far more sweet than that from roots which had grown in moist cool summers. If however the presence of mannite in couch grass is proved, there is still the question whether the mannite always pre-exists in it, which is very doubtful, since, according to Mitscherlich, even those plants which produce mannite, as *Tamarix Gallica* var. *mannifera*, Ehrenb., contain no mannite, but only grape-sugar. It is therefore more than probable that the mannite is a product of the decomposition of this grape-sugar. It would be interesting to examine roots of couch grass in various stages of maturity, and grown under different conditions, as to the amount of grape-sugar and mannite.—Liebig's *Annalen*, Sept. 1846.

Sulphate of Magnesia with excess of Base.

When moderately dilute sulphuric acid is heated with excess of carbonate of magnesia and the solution filtered whilst hot, a sediment separates in the course of some months, which even after long washing parts with sulphuric acid. Dumesnil considers it on this account to be a basic sulphate.—*Archiv der Pharm.*, xlvii. p. 140.

On the Composition of the Oil of Ben. *By* P. Walter.

The oil of ben does not yield, on saponification, any volatile fat acid, but four fixed fat acids, viz. stearic, margaric, and two new acids, which the author calls *benic* and *moringic* acids.

The benic acid occurs in very small quantity in the oil of ben; it consists of $C^{30}H^{30}O^4$, and consequently belongs to the homologous series RO^4, being situated between myristic and ethalic acids. It crystallizes from its alcoholic solution in very voluminous tufts, and fuses at 126°–127°. Benic æther is very soluble in alcohol, and

is deposited from the solution as a crystalline mass, but not in distinct crystals; it melts at a very low temperature, even by the heat of the hand, and contains $C^{34}H^{34}O^4$; it is isomeric therefore with margaric acid.

The other new acid, obtained by the saponification of the oil of ben, has been called moringic acid, from the name of the plant (*Moringa aptera*) which yields the oil. It is liquid, colourless or somewhat yellowish, and contains $C^{30}H^{28}O^4$, that is to say, 2 equivs. of hydrogen less than benic acid. From its composition it appears to be homologous to oleic acid. It would be interesting to ascertain whether, like the last, it would be decomposed under the influence of fusing potash into two acids of another homologous series. Its density is 0·908, its taste insipid and irritating, its smell faint; it reddens litmus-paper, and is very soluble in ordinary spirit even in the cold. It solidifies at 32° F. It is decomposed by sulphuric acid on the application of heat.

M. Walter has verified the composition of this new acid by an analysis of the æthers it yields with alcohol and wood spirit.—*Comptes Rendus*, xxii. p. 1143.

On some Combinations of Manganese with Sulphur.
By A. Völker.

I. *Sulphuret of Manganese and Potassium.*—When anhydrous protosulphate of manganese is fused in a crucible with one-fifth of lamp-black and three times its weight of carbonate of potash and sulphur, employing first a gentle heat, until the carbonic acid has been expelled from the carbonate of potash and converted into sulphuret of potassium, then increasing the heat to a bright red, a fused mass is obtained on cooling, which, after the excess of sulphuret of potassium has been extracted with water, leaves behind large dark red laminæ, aggregated in crystalline masses, which like mica may very readily be separated into thin, transparent, dark red plates.

This combination cannot be obtained pure from commercial manganese; but if pure prepared peroxide of manganese or pure protocarbonate is employed instead of the sulphate, the compound is obtained equally pure. A large excess of sulphuret of potassium and a high temperature are requisite for the success of the operation.

These laminæ have a brownish-red colour; when held to the light they are transparent, with a garnet-red colour, and exhibit a bright lustre as long as they remain unoxidized. They readily oxidize when exposed to the air in a moist state, becoming black and opake, but in a perfectly dry state they may be long preserved. They are nearly insoluble in water, alcohol and æther, and explode violently with nitre. They dissolve entirely in acids, even in dilute acetic acid, with a lively evolution of sulphuretted hydrogen. When heated on platina they become coated with a green powder (oxysulphuret), which protects the interior from further oxidation. They are gradually decomposed by washing with water containing air; the water then extracts sulphate of potash, sulphuret of potassium, and hypo-

sulphite of the protoxide of manganese, leaving behind sulphur and oxide of manganese. The wash-water has an alkaline reaction; dilute acids liberate from it sulphuretted hydrogen, with simultaneous elimination of sulphur. Salts of barytes and acetate of lead produce white precipitates in it; nitrate of silver yields one which appears at first white, but quickly becomes reddish-brown, and at last black; it is therefore requisite, in preparing this compound, to effect the washing with as little access of air as possible, and with boiled water. It is obtained less decomposed by removing the excess of sulphuret of potassium, at first by alcohol, then extracting the sulphate of potash formed in the melting with boiled water, and expelling the water by alcohol, and the latter by æther. The laminæ are then pressed between blotting-paper, dried, and weighed under the air-pump over sulphuric acid. Notwithstanding these precautions, I did not succeed in obtaining a perfectly undecomposed preparation.

The analysis of this combination shows that it is composed of 3MnS + KS. It consists in 100 parts of—

	Found.	Calculated.
Manganese	44·738	44·458
Sulphur	33·091	34·524
Potassium	20·480	21·018

II. *Sulphuret of Manganese and Sodium.*—This combination was obtained, in the same way as the preceding, with carbonate of soda, in the form of minute, shining, bright red acicular crystals, which are insoluble in alcohol and æther, but dissolve entirely with disengagement of sulphuretted hydrogen in dilute acids; they also dissolve in aqueous sulphurous acid, with separation of sulphur and formation of the hyposulphite of the protoxide of manganese. They may be preserved undecomposed in the dry state, but in moist air they are very rapidly oxidized. They burn, when heated upon platina, with formation of sulphurous acid, leaving behind oxide of manganese and sulphate of soda. When they are washed immediately with distilled water, the crystals become oxidized very rapidly, opake, and of a darker colour; if they are now placed in this state, without any application of heat, over sulphuric acid under the air-pump, as soon as they have become dry to a certain extent they absorb oxygen with a considerable disengagement of heat, so that they frequently ignite and burn like a pyrophorus with incandescence.

This combination is represented by the formula 3MnS + NaS, and contains—

	Found.	Calculated.
Manganese	49·11	48·6
Sulphur	37·18	37·8
Sodium	13·26	13·6

III. *Flesh-red Sulphuret of Manganese.*—Great uncertainty still prevails respecting the nature of the sulphuret of manganese formed in the moist way, which induced me to make some experiments with it. It is sometimes considered as an hydrated sulphuret of manga-

nese, sometimes as a combination of protoxide of manganese with sulphuretted hydrogen. Such a combination, if it contained 1 equiv. water or sulphuretted hydrogen, should yield 17·09 per cent. water.

The sulphuret of manganese, precipitated from a protosalt by sulphuret of ammonium, cannot be dried without decomposition; I therefore employed a sulphuret of manganese, which is obtained when sulphuretted hydrogen is passed for a considerable length of time into a neutral solution of the acetate of the protoxide of manganese. Prepared in this way, it has a beautiful red colour, which is sometimes pale, sometimes intensely red; it may be washed without any perceptible decomposition and with a little caution does not change its colour on drying. It dissolves even in dilute acetic acid, leaving a residue of sulphur; on this account, therefore, very little sulphuret of manganese is obtained by passing sulphuretted hydrogen through a neutral solution of the protacetate, as a small quantity of free acetic acid prevents the further precipitation. To procure larger quantities of this sulphuret of manganese, I have evaporated the liquid filtered from the precipitated sulphuret until the whole of the free acetic acid was expelled, and then passed sulphuretted hydrogen again through the solution. I purposely avoided saturating the free acetic acid with an alkali, as the simultaneous presence of sulphuret of potassium favours exceedingly the decomposition of the hydrated sulphuret of manganese. I obtained it of a most beautiful and intense red, almost of the appearance of minium, on precipitating it by sulphuretted hydrogen gas in the light of the sun. On passing sulphuretted hydrogen gas for a length of time through a solution of the protacetate, some sulphuret is deposited on the glass at the margin of the liquid of a far deeper red colour than the first-formed precipitate. On analysis this combination was found to consist of—

	Dark.	Pale-coloured.
Manganese	60·45	59·09
Sulphur	37·68	38·33
Water	2·08	2·44

This sulphuret is not wholly insoluble in water; that it dissolves in colourless sulphuret of ammonium is known; but even in the yellow sulphuret it is not entirely insoluble; and the bicarbonate of the protoxide of manganese, dissolved in water, is not precipitated by sulphuret of ammonium.—Liebig's *Annalen*, lix. p. 35.

Experiments on Glucose and Fruit-sugar. *By* E. Soubeiran.

The analyses which the author has made of fruit-sugar dried at 212° confirm the formula deduced from the experiments of Mitscherlich, $C^{12} H^{12} O^{12}$. This sugar exhibits some very peculiar optical properties. It exerts its rotatory power towards the left, instead of deviating the plane of polarization of the rays to the right, as cane-sugar and glucose do; it preserves this property even when brought to the solid state by evaporation in the water-bath.

M. Soubeiran has also analysed the lead compound of glucose and

fruit-sugar; he always found 74 to 75 per cent. oxide of lead after drying at 212°, whether he employed glucose or fruit-sugar. The results of M. Soubeiran lead to the following formula:—

$$C^{12} H^8 O^8 + 8PbO.$$

The combination with lime, prepared either from glucose or fruit-sugar, is very difficult to dry; after remaining for some time *in vacuo*, it corresponded to $C^{12} H^{14} O^{14} + 4CaO$, but after three months *in vacuo* to $C^{12} H^{12} O^{12} + 4CaO$.

The combination of glucose with baryta is very unstable; it is prepared directly with glucose and baryta; an excess of sugar is employed, the salt precipitated by alcohol, and quickly washed. After remaining for three months *in vacuo* it contained

$$C^{12} H^{14} O^{14} + 3BaO.$$

With respect to the combination of glucose with chloride of sodium, it contains, when dried at 212°, $C^{12} H^{12} O^{12} Na Cl$; the salt dried *in vacuo* contains 1 equiv. of water of crystallization. These results confirm the formulæ previously proposed by Erdmann and Lehmann for this product.—*Journ. de Pharm.*, vols. ix. and x.

On the Products of Decomposition of Gelatine by Chromic Acid. *By* A. Schlieper.

The best proportions for oxidizing gelatine by chromic acid are those pointed out by Prof. Marchand*, viz. 2 parts ordinary glue, 8 of bichromate of potash, 15 of sulphuric acid, and 50 parts of water. The amount of sulphuric acid may be somewhat diminished, but not increased, otherwise the operation would not succeed, and nothing but formic acid would be obtained. The glue is first allowed to swell in the water, and the sulphuric acid then added; when the mixture has cooled, it is poured into the retort containing the bichromate in the state of a fine powder; distillation is now commenced, taking care to cool well, and the operation discontinued when the mass begins to swell. The distilled product is turbid, has an acid reaction, and a strong odour of prussic acid, of which it contains a large quantity. It is redistilled over oxide of mercury, collecting only the first portions; as soon as the liquid which passes has lost its aromatic odour and is decidedly acid, it is tolerably certain that all the oily constituents have passed over. The product amounts to from one-fifteenth to one-twentieth of the whole. After having separated the oily portions, the recipient is changed and the distillation continued; a turbid liquid now passes, which contains the volatile acids in solution; it is neutralized with barytic water, and after evaporation the barytic salts decomposed by sulphate of soda, and the soda salts submitted to distillation with dilute sulphuric acid. The product thus obtained is a concentrated aqueous solution of the volatile acids; it has a strong smell of vinegar and cheese. To effect the separation of the acids, the liquid is saturated with car-

* See Chem. Gaz., vol. iv. p. 10.

bonate of soda and evaporated to dryness, the dried soda salt reduced to powder and agitated with dilute sulphuric acid (1 part of acid to 3 of water) in a narrow cylindrical glass. The liquid separates into two strata: one is aqueous, and crystallizes in part; the supernatant one is oily. From the analyses of the author, it results that the latter is a mixture of *acetic* and *valerianic* acids; the crystallizable acid possessed the composition and all the characters of *benzoic* acid.

The *prussic* acid had remained in combination with the oxide of mercury in the form of a basic cyanide = HgCy + HgO, which has been described by Berzelius in his 'Manual of Chemistry,' vol. iii. p. 871.

The author has established the identity of the preceding bodies by analysis.

To extract the volatile oils produced by the action of the chromic acid, the aqueous portions which passed first were repeatedly rectified, each time collecting only the first portions, which were then in their turn rectified. In this way there was finally obtained an aqueous liquid, upon the surface of which the volatile portion had separated in the form of an oil; the water was saturated with chloride of calcium, decanted, and rectified over fused chloride of calcium. This oil contains two peculiar bodies, which are separated by the difference in their boiling-point.

Valeronitrile is the least volatile oil, very fluid, limpid and colourless; it is lighter than water, and has a density of 0·81; it dissolves to some extent in water, and distils readily with the vapour of water; it is neutral, and possesses an acrid aromatic taste; its odour resembles that of oil of bitter almonds, or of hydruret of salicyle. It burns with a white luminous flame, and is composed of $C^{10}NH^9$. Hydrochloric and nitric acid have no action upon it, but sulphuric acid converts it into valerianic acid, which is set free, and into sulphate of ammonia. It is not altered by ammonia. It dissolves in alcohol and æther in every proportion, and it boils at 257° F. It is attacked by chlorine and bromine when exposed to the rays of the sun.

Valeracetonitrile is a volatile oil of a similar odour to the preceding substance, but more agreeable. It boils betwixt 154° and 158° F.; its density is 0·79; its taste is acrid. On analysis it was found to correspond to $C^{26}H^{24}N^2O^6$.

Ammonia, hydrochloric and sulphuric acids do not alter it, but concentrated sulphuric acid decomposes it in a similar manner to the preceding body, and there is formed sulphate of ammonia, while acetic and valerianic acids are set free.

When chlorine is passed into it the liquid becomes heated, and on cooling deposits beautiful crystals of a chlorinated compound. Bromine acts in the same manner, giving rise to two bodies, one crystallizing in small needles, the other liquid, and which violently attacks the eyes and olfactory organs.

Towards the end of the distillation of the crude product yielding the two preceding oils, the author obtained a heavy oil, which had the smell of cinnamon; but he was not able to investigate it more minutely, from want of material.—Liebig's *Annalen*, vol. lix. p. 1.

Observations on Glycerine. By F. Rochleder.

The fats are, as is well known, decomposed by the action of strong bases or acids into a fatty acid and glycerine. The following is a new method of preparing glycerine:—When castor oil is dissolved in absolute alcohol, and a current of dry muriatic gas passed through the warm liquid, the fat is decomposed. If, when the muriatic acid gas has acted sufficiently long, the liquid be shaken with water, an emulsion is obtained, which soon separates into an oily supernatant, and into a strongly acid aqueous layer. The latter was separated from the layer of oil by means of a siphon, and evaporated in a platinum dish in the water-bath. At first a large quantity of muriatic acid passes off, and there finally remains a yellow syrupy mass. When this is treated with æther, a portion dissolves, while the remainder is not acted upon by the æther. After the evaporation of the æther an oily substance remains, which consists of the combinations of the fatty acids of the castor oil with oxide of ethyle; the substance insoluble in æther forms, after drying *in vacuo*, a slightly yellowish syrup, which has all the properties of glycerine. The oxide of glyceryle of the fats contained in the castor oil has consequently been replaced by oxide of ethyle, while it has combined with the water which the alcohol parted with on its conversion into æther. —Liebig's *Annalen*, August 1846.

Decomposition of the Oil of Sabina by Sulphuric Acid.

When, according to Winckler, oil of sabina is mixed with sulphuric acid, there is formed an oil which is in no way to be distinguished from *Oleum thymi æther*. 1 oz. oil of sabina and the like quantity of sulphuric acid yielded, on distillation with hydrate of lime, 2 drms. of the new oil.—Buch. *Rep.*, xlii. p. 330.

ANALYTICAL CHEMISTRY.

On the Mode of Testing the Presence of Minute Quantities of Alcohol. By Robert D. Thomson.

The determination of the presence of minute quantities of alcohol is a chemical point of some importance, especially in judicial cases. The usual method hitherto adopted for detecting alcohol in mixed fluids, is to subject the fluid suspected to contain it to distillation at a temperature not greater than that which is required to cause the alcohol to pass over into a receiver, and then to judge of the presence of spirit by the vinous odour of the distilled fluid. When alcohol in the form of gin, whisky or brandy, &c. has been swallowed, if death takes place within a short period of the introduction of the fluid, the odour of the spirituous liquors will be distinctly perceptible

to one inspecting the interior of the stomach; but if a considerable time should elapse, as for example a few hours, between the introduction of the spirit and death, it is rarely found that the smell can be detected. Again, if the person should die under the influence of spirituous liquors, and the stomach were not examined within a limited period, the odour of alcohol might not be perceptible, since, as absorption goes on for several hours after death, and as volatile fluids appear to be peculiarly susceptible of rapid absorption, the whole of the alcoholic fluid might be removed from the intestinal canal into the circulation. It has been affirmed that alcohol has been detected in the brain of gin-drinkers; but as the mode of testing adopted was merely the impression made upon the nerves of smell, we may perhaps be allowed to doubt the accuracy of the experiment. It has also been affirmed that the gin obtained from the brain has been inflamed; and if this were correct, we should then be entitled to quote nasal and ocular proofs of the presence of alcohol in the brain; but as the gin of the shops is so weak, that in its natural state it will scarcely burn, we may also be permitted to be sceptical in reference to this second proof*. These views do not tend to disprove the possibility of the presence of alcohol in the vessels of the brain and other portions of the body, because we know that hydrocyanic acid passes to the very extremities of the body, and can be distinctly detected by its odour, until it has either been removed from the system by the combustion of respiration, or simply by exhalation from the lungs. Now alcohol and hydrocyanic acid are somewhat analogous in a chemico-physiological point of view, as they possess a powerfully sedative effect upon the system, are exceedingly volatile, readily absorbable, and require much oxygen to resolve them into simpler forms. For these reasons it appears highly probable that alcohol may be capable of detection in the vessels of the system when it has been swallowed in large quantities. The experiment could only however be made on the inferior animals, and we should require some more definite test than the mere smell of the alcohol. There are other circumstances, in a judicial point of view, in which it may be of importance to detect minute quantities of alcohol; for example, to distinguish small portions of the liquid preparations of opium. In medicine there are used the solution of opium in alcohol, the solution of opium in wine, the solution of opium in alcohol with benzoic acid and ammonia, the solution of opium in vinegar, and lastly the solution in water. When these preparations are entire, there is not so much difficulty in their discrimination; but if they have been exposed to the air, much of the alcohol escapes, and they may all become analogous to a solution of opium in water. To distinguish those which contain alcohol from those which do not, enables us to divide them into two classes, and

* Dr. Percy detected alcohol by means of its inflammability and power of dissolving camphor, after digestion with carbonate of potash, in the brain, bile, contents of the stomach and urine of dogs, into the stomach of which alcohol had been introduced, also in the urine of a man after taking whisky. It has also been found by Dr. Wright in the urine after the use of whisky.—Ed. *Chem. Gaz.*

thus to simplify the inquiry. For these, and many other cases where minute detection is necessary, I have been in the habit for some years of employing a method which depends upon a well-known fact, the dehydrogenation of alcohol by means of oxygen. For this purpose, the fluid to be tested, if coloured or a mixed one, is to be distilled in the water-bath until one-third of it passes over. Should the liquor contain any acetic acid, this may be saturated previous to distillation with carbonate of soda, in order to remove the vinegar smell, which might interfere with the odour of the subsequent test. Into the distilled liquor supposed to contain alcohol should be dropped a crystal or two of chromic acid, and the liquor stirred. If the smallest quantity of alcohol is present, the green oxide of chrome will begin to be disengaged, and at the same time the smell of aldehyde is distinctly perceptible.

The production of aldehyde from the alcohol depends on the separation of oxygen from the chromic acid, its union with the hydrogen of the alcohol, and their consequent removal in the form of water; the formulæ for the two bodies being—

$$C^4 H^5 O + HO \text{ alcohol.}$$
$$C^4 H^3 O + HO \text{ aldehyde.}$$
$$\overline{H^2} \text{ difference.}$$

By means of this simple test it is possible to distinguish a drop of alcohol in half an ounce, and even in an ounce of water. When chromic acid is not at hand, the experiment may be made with bichromate of potash and sulphuric acid. This perhaps affords the most distinct method of performing the experiment, and may be conducted as follows:—Drop a few grains of powdered bichromate into a small flat glass (which tapers towards the bottom) containing the solution to be examined, and add a few drops of oil of vitriol. If alcohol is present, the green oxide will be observed to be developed on the surface of the undissolved salt, and the characteristic odour of aldehyde will speedily be perceptible. As an instance of the utility of this test, it is only necessary to give one illustration. Some months ago I had sent to me by Dr. Joseph D. Hooker, a bottle containing 7 cubic inches of a fluid which was obtained from a species of Eucalyptus, or gum-tree, in Van Diemen's Land, and which is drunk by the natives as an intoxicating liquor. It possessed a powerful odour of vinegar, so powerful indeed that it overcame every other smell which might be present. On neutralizing it with carbonate of soda, it was found to require 28·6 grs. of this salt to saturate the acid, equivalent to 10·12 grs. of dry acetic acid in the whole fluid. On distilling one-third of the liquor, a fluid came over having a faint odour. When chromic acid was added to it, or bichromate of potash and sulphuric acid, the liquor became green, and the odour of aldehyde was powerfully evolved. This proved the presence of alcohol. On evaporating the liquor in the retort, a small quantity of sugar and needle-shaped crystals remained. The latter, when treated with sulphuric acid, gave out a strong odour of acetic acid. These were satisfactory proofs that

the Eucalyptus sugar is capable of fermentation, and that the alcohol produced from it is convertible into acetic acid—facts which show us that the Australian sugar is not manna or a peculiar, but common sugar.—*Monthly Journal of Medical Science*, Dec. 1846.

Estimation of Ammonia in Urine. *By* Dr. I. E. de Vry. *In a Letter to* Prof. Liebig.

Having had an opportunity of testing the applicability of the sulphate of magnesia to determine the ammonia in an abnormal ammoniacal urine, I wished to use this reagent in the examination of normal urine, the acid reaction of which prevents the formation of the ammonio-phosphate of magnesia. After many fruitless experiments, I attained my object by mixing the fresh urine with bicarbonate of soda, filtering, and mixing with sulphate of magnesia. In a few minutes the characteristic precipitate had formed.—*Ann. der Pharm.*, vol. lix. hft. 3.

On the Precipitation and Separation of Alumina and Peroxide of Iron. *By* Dr. W. Knop.

In the precipitation of the peroxide of iron and alumina by ammonia, and their subsequent separation by potash, it is a matter of common experience that these two oxides are extremely difficult to obtain perfectly free from one another. It was to be expected that a more perfect separation would be obtained if this mutual affinity were destroyed previously by combining one of the two substances with some other body. When the precipitate of hydrated oxide of iron and alumina is boiled with potash with the addition of a suitable quantity of sulphuret of ammonium, until the liquid, which at first appears green, deposits, after being left quiet for a time, some black flakes, and appears yellowish, owing to the formation of a slight excess of sulphuret of potassium, and no longer passes green through the filter, which is very soon attained, the alumina, on subsequent precipitation, is obtained on slow desiccation as a transparent mass, and on quick drying and calcining of such a pure white colour as to leave no doubt of its being extremely pure. If we add to this the observations recently published by Malaguti and Durocher*, with respect to the complete precipitation of alumina, which was found to be most perfect under all circumstances with sulphuret of ammonium, it is evident that these two oxides should, when it is practicable, be directly precipitated with sulphuret of ammonium, the precipitate washed with water containing a little sulphuret of ammonium, and the alumina extracted with potash to which a few drops of sulphuret of ammonium have been added, in order to obtain at once a perfect precipitation and separation of these two bodies.—*Journ. für Prakt. Chem.*, Oct. 9, 1846.

* Chem. Gaz., vol. iv. p. 347.

Test for Strychnine.

Instead of the brown peroxide of lead, Prof. Otto recommends a *very minute* quantity of a solution of chromate of potash. This immediately produces, when added to the solution of the strychnine in concentrated sulphuric acid, the splendid violet colour, which is far more distinct and beautiful than on the addition of the brown peroxide of lead.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Experiments and Observations relative to Gun-Cotton.

In a former number of this Journal* we gave a short account of the discovery and preparation of this new explosive substance; as was to be expected, it has continued to form a subject of the greatest interest, and scarcely a week has passed without making us further acquainted with some of its remarkable properties, notwithstanding the danger attending its examination. In the following article we propose to notice only those papers which have since appeared which seem to add to our knowledge of this remarkable substance. We have already stated that paper and other ligneous substances yield an equally explosive compound. According to M. Pelouze†, the *azotic paper* is quite as efficacious in its projectile force as gun-cotton. It is said to leave no residue when well-prepared, to diffuse no nitrous vapour, and not to corrode the fire-arms. M. Pelouze gives the following directions for preparing this paper:—Sheets of paper are immersed one by one in concentrated nitric acid (1·5) for a few minutes, and removed *successively* to be well washed with plenty of water. If the paper becomes disintegrated or contains much foreign matter it should be rejected. M. Pelouze concludes his communication with the following observation:—"When we see nitric acid enter into combinations in which it becomes deprived of its ordinary properties, odour, causticity and solubility, the question suggests itself, whether we may not some day obtain alimentary substances by causing nitrogen to combine with substances which naturally contain none—a discovery from which in my opinion we are not far distant."

To this question a partial answer has already been given, in as far as relates to xyloidine, by Messrs. Bernard and Barreswil, who in a communication to the French Academy at its meeting on the 16th of November, state that they have fed animals with xyloidine, and that it is in no way altered by its passage through the intestine; it remains white, explosive, insoluble in water, soluble in acetic acid and in alcohol, and merely becomes coated with a layer of mucus.

* For November 1, 1846. † Comptes Rendus, Nov. 2, 1846.

In the following number of the 'Comptes Rendus' (Nov. 9), M. Pelouze states that the explosive force of this new compound, either in the form of cotton or paper, is, according to the experiments of M. Prelat, nearly four times greater than that of gunpowder, weight for weight. (According to M. Arago, the relation is as 1 to 3.)

The same number of the 'Comptes Rendus' contains an interesting account of numerous experiments made at the *Direction des Poudres et Salpetres* on the mode of preparing the fulminating cotton, and on its physical and projectile properties, by M. Susane, Captain of Artillery, in which we are made acquainted with some of the disadvantages attending its use. Among these are its bulk, and consequently the difficulty of manufacturing and transporting it, but especially the large quantity of water which is formed on its deflagration, which renders it necessary to cleanse the barrel each time. Moreover, the linen with which it is cleansed is blackened, either by a small quantity of unburnt carbon or by some product resulting from its corrosive effect upon the metal.

With respect to the manufacture of this article, the author recommends that cleansed cotton should be immersed in a mixture composed of equal parts of concentrated nitric and sulphuric acids for about 10 to 15 minutes, and that in order to prevent accidents, no portion of the cotton should be above the level of the liquid, and that it should be dried slowly, and a temperature higher than 212° carefully avoided, especially while still moist. By washing it in water saturated with nitre its energy is slightly increased, but probably not in proportion to the additional expense.

The next paper we have to notice is one by M. Pelouze*, which, as it will prove peculiarly interesting to the chemist, we prefer giving in the author's own words:—

"On a former occasion, when noticing the discovery of this new explosive material, supposing it to be the product of nitric acid upon cellulose (cotton, paper, lignine, &c.), I observed that it was undoubtedly the combustible substance which I described in 1838, and which must contain more oxygen, and consequently more nitric acid, than the xyloidine of M. Braconnot, *i. e.* the pulverulent and amorphous substance which that chemist discovered on precipitating by water a solution of starch made in the cold, or one of cellulose effected at a higher temperature. This has proved to be the case. In the following I shall attempt to show that the xyloidine of M. Braconnot, and the substance which I obtained by impregnating various ligneous substances with concentrated nitric acid are not identical, as I long believed with chemists in general. I shall call *pyroxyline* or *pyroxyle* the product of monohydrated nitric acid upon cotton, paper and ligneous substances, when this action has taken place without having caused the solution of the cellulose; *xyloidine* will henceforth designate the substance obtained by M. Braconnot by precipitating the nitric solution of starch and other ligneous substances.

* Comptes Rendus for Nov. 16, 1846.

" The following are the differences observed between these two substances :—Xyloidine is very soluble in nitric acid, and this solution, which is quickly effected, becomes decomposed in the course of a day; the xyloidine is then converted into a deliquescent acid, which I described eight years ago; pyroxyline does not dissolve even in a considerable excess of nitric acid; it may be left in it for days without disappearing and without any loss in weight. Xyloidine, although very inflammable and detonating when struck, leaves when heated in a retort a considerable residue of carbon; pyroxyline, it is well known, behaves quite differently. When heated from 347° to 356° F., it explodes violently, and its distillation in a retort is physically impossible. Xyloidine may be analysed, like all other organic substances, by means of oxide of copper; pyroxyline, under the same circumstances, breaks the tubes even when quantities 100 times smaller are employed *. 5 milligrms. of pyroxyline, heated in a tube full of mercury, produced a violent detonation; while quantities far more considerable of xyloidine may be decomposed in this way without danger. 100 parts of dry starch, dissolved in concentrated nitric acid, and precipitated by water immediately on its solution, which is very rapid, yield at the most 128 to 130 parts of xyloidine; 100 parts of cellulose (cotton, paper) yield, either after a few minutes or after several days' immersion in monohydrated nitric acid, 168–170 parts of dry pyroxyline. These two experiments are the more characteristic, as the acid liquids, which rest above the pyroxyline and the xyloidine, contain none, or but mere traces of organic matter.

" Eight years ago I determined the composition of xyloidine; I concluded, from my analysis, that it might be represented by 1 equiv. of starch which had lost 1 equiv. of water and had taken up 1 equiv. of nitric acid; I still believe this composition to be correct. However, xyloidine is amorphous and insoluble in water; it is derived from a substance which is never perfectly pure, and which is likewise amorphous and insoluble; and at present we possess no means of judging of the degree of purity of a substance occurring under such unfavourable conditions; it is possible therefore that xyloidine and pyroxyline contain one and the same substance, the properties of which are more or less masked by the presence of some foreign, hitherto unknown substance. The point upon which I insist is, that

* Gun-cotton has however be enanalysed by Mr. Ransome of Manchester, by burning it with oxide of copper in an ordinary combustion-tube. The author states in his paper, which was read before the Literary and Philosophical Society of Manchester, on December 1st, that it yields 26·28 per cent. C, 3·16 H, 60·36 O and 10·20 N, leading to the formula C^{12} H^8 O^{20} N^2. From these results it would appear that gun-cotton is formed from ordinary cotton by the abstraction of 2 atoms of hydrogen and the addition of 3 atoms of nitric acid. Supposing the formula arrived at by the author to be correct, gun-cotton on its explosion would be converted into 12 atoms of carbonic oxide, 8 atoms of water and 2 atoms of nitrogen. This interesting paper will be found entire in the Philosophical Magazine for January.

On the 7th of December M. Peligot communicated a paper to the French Academy which does not confirm the above results. According to M. Peligot, cotton on its conversion into gun-cotton loses 1 equiv. water and combines with 3 equivs. nitric acid, and on its decomposition yields 9CO, $3CO^2$, 3N and 9HO.

the two, compared in the state in which we are at present acquainted with them, differ too considerably to be supposed identical.

"A Dutch chemist, M. Ballot, considers xyloidine to be a mixture of several substances, which have no longer any direct connexion with the starch. Be this as it may, the analysis of this chemist removed the composition of xyloidine from that of pyroxyline far more than mine.

"I selected some samples of cotton and paper, which left but a mere trace of ash; I dried them at 248° F., and submitted them to the action either of monohydrated nitric acid, or to that of a mixture in equal volumes of the same acid and concentrated sulphuric acid. In ten experiments, which lasted from 10 minutes to 48 hours, the increase in weight of the cotton and of the paper was perceptibly the same; it was constantly comprised between 68 and 70 for every 100 parts of the dry cotton or paper. This identity between the cotton and paper, relative to the action of the nitric acid, is not surprising, as paper, excepting traces of foreign matters, is nothing more than cotton the fibres of which have been more or less disaggregated; but what is remarkable in this experiment is the constancy of the results, the rapidity with which the combination takes place notwithstanding its insolubility and that of the cellulose; it is, in fact, a true atomic relation between the elements of a combination effected by mere impregnation and under unusual circumstances. Admitting, what appears to be true, that nitric cellulose is the sole product which originates in the preceding reaction, calculation indicates that it must result from the combination of 2 equivs. monohydrated nitric acid with 1 equiv. cellulose minus 1 equiv. water, and that it is consequently represented by the formula

$$C^{12} H^{9} O^{9}, 2NO^{5}, HO;$$

or, without hypothesis, $C^{12} H^{11} O^{22} N^{2}$. This composition corresponds to the numbers—

Carbon	26·66
Hydrogen	3·70
Oxygen	59·28
Nitrogen	10·36

"The formula deduced from the analysis of xyloidine yields—

Carbon	34·80
Hydrogen	4·34
Oxygen	54·09
Nitrogen	6·77

"Having endeavoured without success to analyse pyroxyline, I employed to determine the composition of this substance an indirect method, which I believe however to be unobjectionable. Having ascertained that 100 parts of cellulose yield on an average 169 parts of dry inflammable substance, I neutralized the whole of the acid liquor in which I had immersed the cotton, and concentrated the resulting nitrate of ammonia in a glass retort, to which I had adapted a tube for collecting the gases. The nitrate of ammonia was decomposed, just as if it were pure, into nitrous oxide and water; I

was not able to detect the presence of carbonic acid in the gases, whence I concluded that no other organic substance was formed at the same time as the nitric cellulose; and as no gas is disengaged in its preparation, it may be concluded that it has, in fact, the composition above indicated. In summing up the preceding observations and experiments, I think I am able to establish in a positive manner that xyloidine and nitric cellulose differ not merely by their properties, but also by their composition. I had considered, with all chemists, that there were merely some slight differences between these two substances, arising from their different degree of cohesion and resistance to solvents, similar to what is manifested between starch and cellulose, as proved by M. Payen; but this is not the case; they are in reality two bodies, possessing different compositions and properties."

The author then offers some remarks on the expense of preparing the new substitute for gunpowder, and enters into a discussion of the history of its discovery, summing up as follows:—"Xyloidine and pyroxyline are, as far as we are acquainted with them at present, not identical. M. Braconnot discovered xyloidine; I discovered the singular substance pyroxyline by a process entirely new, and which no one before me had previously suspected; I pointed out its excessive combustibility, and suggested its application in artillery. To M. Schönbein is due the honour of having shown that these substances constitute an explosive material far more energetic than gunpowder. In conclusion, the only method as yet known for preparing this new explosive substance is that which I described in 1838, M. Schönbein having hitherto kept secret both the nature and preparation of his gun-cotton."

Prof. Schönbein declares that his gun-cotton is different from that described by Pelouze, as will be seen from the following letter addressed to the Editor of the 'Times:'—

Sir,—As your widely-circulating paper has taken some interest in the gun-cotton affair, you will perhaps have the kindness to publish the following lines in the 'Times:'—Some chemists have declared my gun-cotton to be Braconnot's and Pelouze's xyloidine, and it was only the other day that the same opinion was expressed in the French Academy. I have more than one reason to deny the correctness of that assertion, and the statement of a very simple fact will be sufficient to bear me out in what I say. Pelouze's xyloidine is, according to the statements of that distinguished chemist, readily soluble in acetic acid, forming with the latter a sort of varnish. The same acid has not the slightest action upon the gun-cotton, however long and at what temperature soever both substances are kept in contact with one another. The gun-cotton exhibits its full weight and explosive force after having been treated with that acid for hours. There are besides other differences between my cotton and Pelouze's xyloidine, which will be made known in their proper time.

I am, Sir, your obedient Servant,

Bâle, Nov. 13. C. P. Schönbein.

The next paper connected with this subject is one by M. Pelouze, on the manufacture of percussion caps from the new material*; it is found, however, that on striking a cap filled with pyroxyline, either in the form of paper or cotton, the combustion is incomplete, and the charge is rarely fired; but on substituting pyroxyline, prepared with very compact tissues of hemp, linen or cotton, cut into small fragments and distributed in copper capsules, the detonation is as powerful as with fulminating mercury.

Gun-cotton, compressed with a few grains of ordinary powder into new capsules, furnishes very excellent percussion caps; the powder determines the combustion of the whole of the pyroxyline, and the fire is readily communicated to the charge. Charcoal and sulphur give equally good results.

The same Number of the 'Comptes Rendus' contains a notice by M. Séguier on its use in the pyrotechnical art. Paper, prepared according to the method described by M. Pelouze, and moistened with solutions of nitrate of strontia, sulphate of copper and nitrate of baryta, yield very beautiful red, green and white fires. The slight retardation in the combustion produced by the immersion in solutions of metallic salts is highly favourable to the duration of the effects sought for in the use of coloured fires.

At the meeting of the French Academy on Nov. 23rd, a paper was communicated, bearing the title, 'Experiments made to apply the expansion produced by the deflagration of Azotic Paper to the movement of Machinery,' but no details are given; and also one by M. Gaudin, who suggests slightly charring the cotton, in order to distinguish it from ordinary cotton. He advises the employment of nitre and commercial sulphuric acid for its preparation. Nitrate of soda was not found to answer.

At the same sitting M. Dumas communicated the following observations on this subject:—

"He had convinced himself that the analysis of gun-cotton might be easily effected by means of the apparatus employed by Gay-Lussac and Thenard forty years ago in the analysis of organic substances. The combustion tube is heated over an alcohol lamp from 400° to 600°, little pellets of the gun-cotton are dropped into it, and burn very lively and without the least danger. They yield aqueous vapour, carbonic acid, carbonic oxide, and, as was to be expected, a large quantity of nitrous vapour and binoxide of nitrogen. The crude gas contains sufficient inflammable products to burn when a candle is brought near: the colour of the flame indicates the presence of some compounds of cyanogen†.

"If the explosion of the gun-cotton yields such gaseous products, the fire-arms cannot resist, but must soon become oxydized. It is evident however that the deflagration of this substance must yield very different products when it takes place under the pressure of

* Comptes Rendus, Nov. 16.

† This, as the reader is aware, had already been observed by Messrs. Teschemacher and Porrett, in their communication to the Chemical Society, Nov. 16. See this journal, p. 496 of the preceding volume.

the projectile in a narrow space, where for some time the inflammable gases and the nitrous vapour strongly heated may react one on the other. Thus so far as concerns fire-arms the use of the gun-cotton may not be attended with those inconveniences which the acid products of its explosion in the open air might lead us to expect. However, gun-cotton immersed in an aqueous solution of nitre and then dried yields less nitrous vapour, so that probably this injurious property may be modified by some additions."

M. Dumas then stated that M. Bizard had recently made some experiments which might prove of great value in the discussion of these new subjects, and the accuracy of which he had confirmed: cotton impregnated with chlorate of potash yields a fulminating substance which is perhaps superior to ordinary gun-cotton. 40 to 50 millegrammes of cotton thus prepared sufficed for the charge of a pistol, and produced an effect which could not be exceeded without the danger of bursting the barrel. Sawdust mixed with the same salt affords an explosive mixture of similar power.

Gun-cotton has also been analysed by Fordos and Gelis * by passing the gases generated on its combustion into a solution of nitrate of silver, in which they caused a considerable precipitate which possessed all the characters of cyanide of silver. The authors are led to believe that it is in the state of hydrocyanate of ammonia, as the product which precipitates the nitrate of silver appeared to condense in the cold parts of the apparatus, and the odour which is disengaged during the experiment does not resemble that of prussic acid. The gases produced on the combustion of gun-cotton are colourless, and the atmosphere of the retort only assumes the red tint peculiar to hyponitric acid when mixed with air; it is therefore the deutoxide of nitrogen which is formed, and the nitrous vapours indicated by other experimenters result from the action of the oxygen of the air upon this compound. In conclusion, besides the water and nitrous vapours which have already been pointed out as disadvantages, there is formed a considerable quantity of a cyanic compound; without exaggerating the importance of this result it will be necessary not to lose sight of it in the various applications that may be made of this remarkable substance.

Analysis of some Alloys employed in the Arts. *By* M. Louyet.

I received three specimens of German silver, of different quality, which are employed at Birmingham in the manufacture of cutlery and dinner-services. This branch of industry has acquired great development since the discovery of the galvanoplastic application of the precious metals; and the use of electro-plated German silver services has become very general in England. I was informed that these alloys must vary considerably in composition, for they were sold at very different prices. Qualitative analysis however showed that all three contained only copper, nickel, some zinc, and slight

* Comptes Rendus, Nov. 23, 1846.

traces of iron. The quantitative analyses were made by dissolving 2 grms. of the alloy in nitric acid, evaporating the solution to dryness, in order to expel every excess of acid, redissolving the residue in hydrochloric acid, diluting the liquid with a large quantity of water, and then passing through it a current of sulphuretted hydrogen. The sulphuret of copper was thrown upon a filter, and washed with water containing a small quantity of sulphuretted hydrogen in solution. The filter and the sulphuret were heated to redness in a platinum crucible. By means of a blowpipe a gentle current was directed on to the mass until it no longer gave off any blue flame. The residue was now digested with hot nitric acid, the liquid diluted, filtered, boiled, and precipitated by a solution of caustic potash. The precipitate of binoxide of copper was edulcorated until the wash-water, evaporated on a bright blade of platinum, exhibited no residue. The filter and the oxide were then heated to redness in a platinum crucible. After cooling, the mass was moistened with a few drops of nitric acid to peroxidize the protoxide of copper, and also the metallic copper reduced by the paper of the filter; it was then gradually heated to redness, and the oxide quickly weighed. From the weight of the latter that of the metallic copper contained in the alloy was calculated.

The liquor separated by filtration, and containing the zinc and nickel, after boiling to expel the sulphuretted hydrogen, was supersaturated with a solution of carbonate of soda. To separate the zinc from the nickel, instead of employing the method described at such length in the analytical chemistry of Rose*, I wished to test the process proposed by Mr. J. D. Smith †.

To separate the metals, according to this chemist, the two oxides are converted into acetates; an excess of acetic acid is added to the solution, through which a current of sulphuretted hydrogen is passed, which precipitates the whole of the zinc in the state of sulphuret, while the oxide of nickel remains in solution. Having finally obtained the oxides of nickel and zinc in the state of hydrates, after having boiled them for some time with an excess of carbonate of soda in order to decompose any subsalt of zinc that might have formed, the washed hydrates were dissolved in an excess of pure acetic acid and heated; a current of sulphuretted hydrogen was then passed into the cold liquid until it smelt strongly of it; the zinc was precipitated perfectly white; it was collected on a filter, well washed, and digested on the filter with some weak muriatic acid, the liquid warmed, filtered, and finally precipitated by solution

* By this method the zinc and the nickel are precipitated in the state of oxides, well washed, and heated to redness; the oxides are then placed in the bulb of a reduction tube, which communicates on the one hand with an apparatus from which dry muriatic gas is liberated, and on the other with a little flask containing a very dilute solution of ammonia. As soon as the air is expelled, the bulb is gradually heated to redness, the oxides are converted into chlorides, the chloride of nickel remains in the bulb, and the volatile chloride of zinc passes into the solution of ammonia, in which it dissolves. The oxides are then determined by the usual processes. This method yields very accurate results.

† Philosophical Magazine, 1836, vol. viii. p. 80.

of carbonate of potash with all the necessary precaution. The oxide of zinc was collected on a filter, edulcorated, ignited in a platinum crucible and weighed. The liquid filtered from the sulphuret of zinc was precipitated by caustic potash, and the precipitated hydrate of nickel washed, ignited and weighed. The following are the results of the analysis:—

	I.	II.	III.
Copper	63·34	62·46	62·63
Nickel	19·13	15·05	10·85
Zinc	17·01	22·15	26·05
Loss	0·52	0·47	0·47

The proportion of copper is nearly the same in the three alloys; the nickel appears to be in the relation of 2 to $1\frac{1}{2}$ and 1, and the zinc as 1 to 1·3 and 1·5. To check my analyses, I examined the method of separating nickel and zinc proposed by Mr. Smith, which I had followed, as to its accuracy.

When a current of sulphuretted hydrogen is passed into the solution of a neutral salt of zinc, this salt is partially decomposed and sulphuret of zinc precipitated; but the action stops when the liquid has become acid to a certain degree. However, it is stated in Berzelius's Manual that acetic acid forms an exception to this rule, the acetate of zinc being entirely decomposed. I took a solution of pure chloride of zinc, mixed it with a solution of pure chloride of nickel, added an excess of carbonate of soda to the liquid, and boiled it for a considerable time. This precaution is indispensable to prevent the precipitated hydrated oxides containing zinc in a state of subsalt. The washed oxides were dissolved in an excess of acetic acid, and a continuous current of sulphuretted hydrogen passed into the solution. The sulphuret of zinc was thrown down of a slightly yellowish-white colour, which proves that no trace of a salt of nickel had been decomposed, otherwise it would have been black, or at least brown. The sulphuret of zinc was collected on a filter, and a fresh current of sulphuretted hydrogen was passed into the liquid; as no precipitate was formed, I concluded that the whole of the salt of zinc had been decomposed. The liquid containing the nickel was boiled to expel the sulphuretted hydrogen, an excess of pure solution of potash added, heat applied, and then filtered; the filtered solution did not yield the least precipitate with hydrosulphate of ammonia. The precipitated oxide of nickel was thoroughly washed, dried and calcined; it was then treated by the method described by Rose for separating nickel from zinc; but not the least trace of chloride of zinc was volatilized, and the ammonia in which was collected the muriatic acid gas contained absolutely no trace of a metallic salt. It is perfectly established therefore that the process of Mr. Smith for the separation of nickel and zinc yields very accurate results, and will undoubtedly supersede the old process, which requires considerable time and a somewhat complicated manipulation. —*Bulletin de Musée de l'Industrie*, 1846.

Mode of ascertaining whether Olive Oil has been sophisticated with Rape or Poppy Oil. By M. Diesel.

Pure olive oil is coloured green by ordinary nitric acid. On the other hand, 1 drm. of olive oil, sophisticated with rape oil and mixed with 12 drops of nitric acid, exhibited a strong yellowish-gray colour. Comparative experiments with various mixtures of oil showed that this reaction was still perceptible even with the addition of one-tenth. The adulteration with poppy oil is likewise easily detected with nitric acid, but the mixture then becomes yellowish-white, and not brownish as in the previous case. Pure nitric acid exhibits the reaction in a far less degree. Dr. Bley adds, that the samples must be judged of in the course of 12 hours after the addition of the nitric acid, as pure olive oil is likewise coloured more or less brown after a longer interval.—*Archiv der Pharm.*, xlvi. p. 287.

REVIEW.

Elements of Chemistry. By Thomas Graham, F.R.SS. L. and E., &c. &c. Second Edition, entirely revised and greatly enlarged. Part I. London, Baillière.

Chemists and natural philosophers will be alike gratified by the appearance of the first part of the second edition of Mr. Graham's 'Chemistry.' The clear, concise, yet elegant style of the first edition, which has given to the work a classic celebrity, is rendered, if possible, still more lucid in the Part before us; the chief merit of which, however, consists in the valuable additions which have been everywhere introduced by the author. All the important results obtained from the most recent researches of philosophers, both at home and abroad, have been embodied in the present edition; and these alone render the book indispensable to such as have not opportunities of entering into the minute detail of the original papers.

The author has likewise published (we believe now for the first time) some of the laws elicited by his own laborious experiments upon the effusion and transpiration of gases; and to these we would more particularly direct attention, whilst in passing we point out a few of the more important additions.

In the section upon the expansion of liquids by heat, we find the results of the researches of M. Isidore Pierre corroborating and extending the observation of M. Gay-Lussac, that certain liquids (alcohol and sulphuret of carbon), when compared at the same distance from their respective boiling-points, expand and contract in the same ratio by the addition or loss of heat. M. Pierre finds the same uniformity in the bromides of ethyle and methyle, and in the corresponding iodides. The law of Mariotte has been modified by the recent exact experiments of MM. Magnus and Regnault, the more easily liquefied gases being found more expansible by heat than air.

The table of the specific heat of solid bodies is corrected from the results of MM. Ed. Desains and Regnault, and the table of the specific heat of gases much extended.

Mr. Hutchison's practical table, showing the conducting power of the various materials used in building, enriches the section on conduction.

An improved method of ascertaining the latent heat of vapour, water, and other liquids, employed by M. Brix of Berlin, has led to results probably the most exact which we possess upon that subject.

The laborious and extensive series of experiments undertaken by M. Regnault to determine the tensions of aqueous vapour *in vacuo* between 32° and 212°, as also his researches upon hygrometry, are duly noticed; and we are happy to inform our readers that a full translation of these very valuble memoirs is about to be presented to the English public in the next Part (Part XVI.) of Taylor's 'Scientific Memoirs.'

We will now advert to the author's own researches upon the effusion and transpiration of gases.

By the effusion or pouring out of gases, Mr. Graham expresses their passage into a vacuum by a small aperture in a thin plate. He finds that the time of passage into a vacuum of a constant volume varies in different gases, the lightest passing in the shortest time. This time corresponds very closely for each gas with the square root of its density; the velocities of passage are consequently in the inverse proportion, or as 1 divided by the square root of the density of the gas.

The passage of gases through tubes of fine bore, of greater or less length, is called transpiration; and as peculiar interest is attached to the investigation of this subject, we beg leave to quote the author's own words:—

"It is found that for a tube of any given diameter, the times of passage of different gases approximate the more closely to their respective times of effusion, the more the tube is shortened and made to approximate to an aperture in a thin plate; while, as the tube is elongated, a deviation from those rates is observed, which is rapid with the first additions in length, but becomes gradually less; and finally, with a certain length of tube, the gases attain rates of which the relation remains constant, or nearly so, for any further increase of length. The same relation in velocity between the different gases is then found to extend also through a considerable range of pressure, as from one to one-tenth of an atmosphere.

"The ultimate rates of transpiration differ considerably from the rates of effusion of the same gases, and have no uniform relation to their density. Of all the gases tried, oxygen passes with least velocity through a capillary tube.

"The effusion of a given measure of air into a vacuum takes place always in the same time, whatever may be its density, from one-fourth of an atmosphere up to two atmospheres. But the transpiration of air of different densities was observed to take place in times which are inversely as the densities; or, the denser air is, the more rapidly is a given volume of it transpired. Hence, the tran-

spiration of air and all gases is greatly affected by variations of the barometer; the higher the barometer, the more quickly are the gases transpired. The difference in this respect separates completely the phænomena of effusion and transpiration.

"Nor can the phænomena of transpiration be an effect of friction, for the greater the density of air, the more should its passage be resisted by friction. The transpirability of a gas appears to be a constitutional property, like its density or its combining volume; and the investigation is of peculiar interest, from supplying a new class of constants for the gases, namely their coefficients of transpiration. The rates of transpiration of different gases were further observed to be the same through a fine capillary tube of copper of 11 feet in length, and a mass of dry stucco, as through capillary tubes of glass."

The exceedingly interesting results of M. Regnault's researches into the specific or atomic heat of compound bodies, whence the law is deduced, that "in all compound bodies of the same atomic constitution, the specific heats are in the inverse proportion of the atomic weights," and an extended table of the specific gravities of gases and vapours, conclude the Part before us. It will be obvious to all, from this short notice, how much the student is indebted to Mr. Graham for the labour bestowed upon this new edition.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Dec. 7, 1846. (The President, Professor Graham, in the Chair.)

"On the Metaphosphates," by Mr. R. Maddrell.

The researches recorded in the present paper resulted from the attention of the author having been called to a new method of preparing phosphoric acid from bone-earth, proposed by Prof. Gregory, and also to a new and apparently anomalous compound of phosphoric acid with magnesia, accidentally obtained in that process.

When phosphoric acid from bone-earth, freed from lime and sulphuric acid, is heated to a temperature above 600° F., it deposits a white substance having the general characters of Dr. Gregory's salt. It contains however 22·47 per cent. of magnesia, corresponding to the metaphosphate of magnesia, instead of 16·28 per cent., the quantity found by Dr. Gregory. On dissolving the residual acid in water, evaporating and again heating, a second quantity of the same substance separated; and it was only after a third repetition of the process that an insoluble substance, containing the proportion of magnesia stated by Dr. Gregory, was obtained. This, on careful analysis, however, turned out to contain soda, being in fact a double metaphosphate of magnesia and soda, $3(MgO, PO^5) + NaO, PO^5$. The residual phosphoric acid still contained traces of magnesia and soda.

Corresponding compounds, containing the oxides of nickel and cobalt in place of magnesia, were prepared by adding the sulphates

of those bases to bone-earth phosphoric acid, evaporating and heating as before. They were insoluble in water and dilute acids, and possessed, the first a greenish-yellow, and the second a rose colour.

By substituting really pure phosphoric acid for that prepared from bones, and following the same mode of proceeding, the metaphosphates of a number of metallic oxides were obtained, as those of nickel, cobalt, manganese, alumina, peroxide of iron, oxide of chromium, oxide of copper, baryta, strontia, lime, magnesia, potash and soda. They are all insoluble, or nearly so, in water, even those of the alkalies, but dissolve with more or less difficulty in acids. They are all anhydrous; the compounds containing protoxides have the formula MO, PO^5, and those of sesquioxides the formula M^2O^3, PO^5.

"On the Amounts of Sulphur and Phosphorus in various Agricultural Crops," by H. C. Sorly.

The author, having thought it probable that the usual method of estimating the sulphur and phosphorus in plants from their ashes was open to error, instituted the series of experiments which form the subject of this communication. The plan followed was by digesting the material in nitric acid, assisted by heat, until the whole of the organic matter was oxidized, and from the clear watery solution of this, ascertaining the weight of precipitated sulphate of barytes, from which the sulphur was estimated. The phosphorus was arrived at through the medium of the quantity of phosphate of lead obtainable. The long series of substances examined, amounting to 66, are arranged in a tabular form, the different parts of the plant being given separately. From these data the author then calculates a second table, giving the quantity of sulphate of lime and bone-phosphate in pounds removed from the acre of land by the crop, the weight of the crop per acre being specified.

"Observations on the Oxidizing Power of Oxygen when disengaged by means of Voltaic Electricity," by Dr. H. Kolbe.

Dr. Kolbe finds that by submitting a concentrated solution of sesquichlorocarbohyposulphate of potash to the action of a voltaic arrangement composed of four elements of Bunsen's battery, having platina electrodes, it is resolved into chlorine, carbonic acid, sulphuric acid and perchlorate of potash, the formation of the latter being preceded by that of chloric acid. When chloride of potassium was substituted, chlorate and perchlorate of potash were also formed even when sufficient sulphuric acid was added to combine with all the potash. When chloride of ammonium was employed, chloride of nitrogen in oily drops was deposited on the surface of the positive platina plate. Dr. Kolbe has not prosecuted the experiments on inorganic bodies further, having obtained results of much greater interest in operating upon organic compounds, the results of which he trusts shortly to lay before the Society.

Dec. 21, 1846. (The President, Professor Graham, in the Chair.)

"On the Existence of a new Vegetable Alkali in Gun-Cotton," by Robert Porrett.

In the paper on the composition of gun-cotton read before the Society on the 7th of December, it was stated that the action of a

small galvanic battery on gun-cotton gave a slight indication of its decomposition. Mr. Porrett, by placing gun-cotton moistened with acetic acid between a plate of silver and of zinc, completing the circle, and leaving it for 48 hours, obtained a small quantity of matter encrusted on the silver plate, resembling starch in appearance, but which powerfully restored the blue colour of reddeed litmus-paper, and when heated to redness left a black carbonaceus residue.

Mr. Porrett then endeavoured to obtain this substance by chemical means in a larger quantity, and, after several trials, succeeded by the following process:—2 oz. by measure of nitric acid of spec. grav. 1·45 were added to 50 grs. of gun-cotton, heated gradually to 100° F., and kept below 180°; the gun-cotton dissolved without any evolution of gas. When a portion of this solution was dropped into water, a white precipitate formed, having all the properties of gun-cotton, structure excepted. On heating the liquid solution to 240°, deep red vapours were given off; these, collected in a receiver surrounded by ice, proved to be hyponitrous acid. The same effect took place when sulphuric acid was used for the decomposition.

The solution of nitric acid when cold was first nearly neutralized by carbonate of potash, and then perfectly neutralized by bicarbonate; the liquid became thickened, not only by the quantity of nitrate of potash formed, but also by an abundant precipitate of a whitish-gray colour, consisting of the new alkali, probably in the state of carbonate. As much of the nitrate of potash as possible was separated by repeated crystallizations; but finding that neither æther, alcohol or spirits of wine would act as a solvent of the alkaline oxide of lignea, it was kept in solution in a small quantity of water, contaminated by a little nitrate and bicarbonate of potash. This aqueous solution containing the new alkali in abundance, very powerfully acted upon reddened litmus-paper; and when a portion of it was neutralized by hyponitrous acid, hyponitrite of oxide of lignine, identical with gun-cotton, was reproduced, and precipitated as an insoluble compound. A new alkali has thus been put into the hands of chemists, which Mr. Porrett proposed to name "Lignea;" it offers a wide field for research as to its properties and combinations with acids, alkalies and halogens. The composition of lignea must be that of lignine plus 2 atoms of oxygen given off by nitric acid in becoming hyponitrous acid; the latter acid and lignea may be employed as mutual tests of each other's presence in fluid combinations.

Mr. Porrett concluded by pointing out the probability of the production of this alkali from the natural decay of woody fibre from leaves and decayed plants, and its combination with acetic acid; and considered that the acetate of lignea so formed may exist in the sap of all vegetable substances, and be decomposed or deoxidized by light acting upon the leaves and bark of trees, reproducing lignine for the assimilation and growth of the plant.

THE CHEMICAL GAZETTE.

No. CII.—January 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Relation between Nitrification and the Fertilization of Soils.
By F. Kuhlmann.

Animal substances exert their salutary influence upon vegetation only when by their decomposition there is a development of carbonate of ammonia. I have adopted the same view for the nitrates employed as manures; I have generally regarded their influence to be effectual only when, by the deoxidizing action of putrid fermentation, their acid is converted into ammonia. To show that this conversion was probable, I was led to examine whether, in operating upon liquid products, it would be possible to obtain results analogous to those arrived at in 1838, with the aid of spongy platinum, in acting upon mixtures of gases or vapours. In the same year I showed that the production of ammonia, by the action of weak nitric acid upon tin, was not an isolated fact, but that it resulted from the action of this acid upon all the metals capable of decomposing water, and consequently the ordinary result of the contact of nascent hydrogen with nitric acid. MM. Fordos and Gelis have confirmed the correctness of my results, to which they have added several other facts, especially that of the decomposition of sulphurous acid by the action of nascent hydrogen.

The following are the results of some further experiments in support of the conversion of the nitrates into ammoniacal salts. When some fragments of nitre are thrown into a mixture of zinc or iron and sulphuric acid, or, what is preferable, weak hydrochloric acid, the disengagement of hydrogen is stopped or retarded until the whole of the nitric acid of the nitrate is converted into ammonia.

Nascent sulphuretted hydrogen occasions a similar conversion, at the same time depositing sulphur.

When a nitrate, the metal of which is precipitated by zinc, nitrate of copper for instance, is placed in presence of a mixture of zinc and hydrochloric acid, for every equivalent of zinc dissolved there is 1 equiv. of copper precipitated, and 1 equiv. of the nitric acid of the nitrate is converted into 1 equiv. of ammonia, the whole without any liberation of hydrogen.

By passing a current of sulphuretted hydrogen through a solution of chloride of antimony mixed with a nitrate, the acid of this latter

is converted into ammonia. Similar metamorphoses are effected by the contact of nitrates with a solution of sulphuret of arsenic in potash, or with the hydrated protoxides of tin and iron.

I think that, after the announcement of these facts, no doubt can remain relative to the decomposition which the nitrates experience in the soil under the influence of putrid fermentation. It is known that this fermentation, considered as a deoxidizing agent, is capable of overcoming the strongest affinities.

If the fertilizing agent must be presented to the plant principally, if not exclusively, in the state of carbonate of ammonia, serious inconveniences arise from the volatile nature of this salt; for it is no sooner confided to the soil to fertilize it, than a large portion is removed by the air to be diffused over the earth.

We have now to examine what influence nitrification has upon vegetation. It is conceivable that the mode of fertilization by the ammonia of the atmosphere may suffice for certain countries, and not for others; the more we approach the meridional countries, the less necessity is there for manures.

If I entertain the conviction that the nitrates do not act generally as fertilizers, except after having experienced, at a certain depth in the soil, a decomposition which yields carbonate of ammonia, I am not the less satisfied that the fertility of the soils likewise depends on an inverse reaction, which is opposed to the volatilization of the ammonia; I mean the conversion of ammoniacal salts into nitrates, which occurs in the superficial portions of those soils which present a suitable chemical composition, and are placed under the most favourable conditions of moisture and temperature.

With respect to the conversion of ammonia into nitric acid, I proved satisfactorily in 1838 that this furnishes the most simple and conclusive explanation of the formation of the nitre beds. My opinions on this subject are at present admitted by the majority of chemists; but if any doubt should still exist, the following results will suffice to remove them. When a mixture of bichromate of potash, concentrated sulphuric acid and sulphate of ammonia is heated in a retort, a large quantity of nitric acid distils over. On heating a mixture of peroxide of manganese or peroxide of lead or minium and weak sulphuric acid in the presence of sulphate of ammonia, the ammonia of the sulphate is equally converted into nitric acid, which passes over.

In investigating the conversion of ammoniacal gas into nitric acid by its contact at a high temperature with the peroxide of manganese, I found that we possessed in this oxide a valuable agent for transferring *indefinitely* the oxygen of the atmosphere to the ammonia. MnO^2 by a first oxidation passes into the state of MnO, which the contact of air immediately converts into $Mn^3 O^4$, which is again susceptible of oxidizing the ammonia.

If we now compare the slow progress of nitrification in the northern provinces with the rapidity with which it results in meridional countries, it will be conceived how much greater the expense in ammonia or in nitrogenous manures must be in the north than in the south.

The Academy will probably attach some interest to the result of the experiments I have made in support of my opinion respecting the influence of nitrification upon the fertilization of soils; it will perhaps also recognise that the facility with which I have succeeded in converting ammonia into nitric acid will serve, in case of any future continental blockade, to render Europe more independent of India and Chili in regard to its supplies of nitrates or nitric acid; that, under other circumstances, by an inverse reaction, we shall find in the nitrates of India and Chili abundant sources of ammonia, turning to advantage the hydrogen, and especially the sulphuretted hydrogen, which at present is lost in many operations of the arts, and moreover proves of considerable injury to the public health.

In conclusion, I may mention that the various reactions, the results of which are noticed in this article, have led me to the two following applications:—1st, I have based a new process for determining the amount of nitric acid and for the analysis of the nitrates, upon the property of these bodies of being entirely converted into ammonia or into ammoniacal salts under the influence of nascent hydrogen; 2nd, by submitting to the action of nascent hydrogen various binary or saline combinations of metals, I have completely reduced a large number of these insoluble or sparingly soluble compounds in weak acids.

By operating upon native crystalline compounds, such as zigueline, azurite, malachite, carbonate of lead, oxide of tin, &c., the metal obtained preserves the crystalline form of the combination in which it existed.—*Comptes Rendus*, Nov. 30, 1846.

On the Conversion of Ammonia into Nitric Acid. By M. Dumas.

When a current of moist air mixed with ammonia is passed over chalk moistened with a solution of potash, the temperature being raised to about 212° F., there is formed in the course of a few days a considerable quantity of nitrate of potash. This experiment, which agrees with all the researches of M. Kuhlmann upon nitrification, I was led to by the observations I have recently made on the conversion of sulphuretted hydrogen into sulphuric acid.—*Comptes Rendus*, Nov. 30, 1846.

Experiments relative to the Theory of Manures. By F. Kuhlmann.

In this investigation I proposed in the first place to examine what consequences may result from the continued use of azotized manures. The results of my experiments establish that the exclusive employment of nitrogenous products upon grass lands over-excites the vegetation at the expense of the following crops; so that there is reason to conclude that the agriculturist is subject to a great loss by exceeding certain proportions in manuring his lands with nitrogenous matters when a single manuring is to suffice for several successive crops.

The second portion of my experiments relates to the influence

upon vegetation of mineral saline substances, and in particular of common salt. The most striking result of these investigations is, that the use of these substances, and in particular of common salt, yields in general favourable results only on moist lands; it may therefore prove useful for the fertilization of certain soils and for certain crops, while for others it will not be of the slightest benefit.

Without doubt agriculturists will derive greater advantage from the use of common salt in the feeding of cattle; and since the stable manures will then contain tolerable quantities of this salt, it will be requisite to be more cautious when distributing it over the land.—*Comptes Rendus*, Nov. 30, 1846.

Action of Iodine upon the Xanthate of Potash and the analogous Salts of the Methyle Series. By P. Desain.

It has been shown by M. Zeise, that when a concentrated solution of xanthate of potash in alcohol is treated with iodine, it is entirely decolorized, and iodide of potassium and sulphur deposited; and that when the supernatant liquid is distilled, sulphocarbonic æther or protosulphocarbonate of the oxide of ethyle may be obtained from it. Quite recently it has been shown by M. Cahours, that the corresponding product of the methyle series or the protosulphocarbonate of the oxide of methyle may be obtained by following very nearly the same process.

Several years ago I likewise had occasion to investigate the action of iodine upon the xanthate of potash, and I found that the immediate product of this action is a readily crystallizable body, which may be represented by the formula $C^2 S^4, C^4 H^{10} O^2$. This substance is insoluble in water, soluble in alcohol, and is decomposed at about 320° F., yielding on distillation xanthic æther, $CS^2, C^4 H^{10} O$.

I obtained perfectly similar results by treating the salts analogous to the xanthate of potash of the methyle and amyle series. I always observed the iodine combine with the metal of the potash, whilst the oxygen of this base was transferred to the bisulphocarbonate of the oxide of methyle or of amyle, yielding the bodies $C^2 S^4, C^2 H^6 O^2$, or $C^2 S^4, C^{10} H^{22} O^2$. These bodies have an oily appearance, and are decomposed on distillation into the corresponding æthers.—*Comptes Rendus*, Dec. 7, 1846.

On Achilleine and Achilleic Acid. By B. Zanon.

To obtain the active principle of this plant, which is used in some parts of the south of Europe as a substitute for sulphate of quinine in cases of intermittent fever, the author boiled 2000 grms. of the dried plant with 16 lbs. of rain water for about 2 hours. The residue was again boiled twice with smaller quantities of water, and the filtered solutions mixed. These were then clarified with white of egg, and evaporated at a gentle heat until a whitish pellicle formed on the surface. After 24 hours the cold liquid had deposited a mass, which consisted for the greater part of

vegetable fibre, green colouring substance, with some coagulated albumen, extractive matter insoluble in alcohol, lime salts and traces of silica. The filtered bitter and acid liquid was treated with an excess of hydrate of lime, which produced a white precipitate; upon this the liquid was treated with acetate of lead as long as any precipitate was formed. This was collected on a filter, and the solution saturated with sulphuretted hydrogen, after which it still possessed a yellowish colour and a very bitter taste. On evaporation it yielded nearly 150 grms. of dry extract, which, as well as the previously filtered sulphuret of lead, was exhausted with alcohol. The two, mixed and evaporated, yielded 130 grms. extract, which the author calls achilleine. As the substance thus obtained still contained some acetate of lime, resin, &c., the author modified the above process, treating the neutralized decoction with animal charcoal, evaporating to dryness, and extracting with boiling absolute alcohol. In this way the formation of acetate of lime was avoided and time spared. The achilleine can be freed from the slight trace of resin by solution in water. The colour of achilleine is instantly destroyed by chlorine; it is not precipitated by tincture of galls nor acetate of lead, but is thrown down by basic acetate of lead; it dissolves in ammonia, and the solution, when exposed to the air until the ammoniacal odour has disappeared, deposits brown flakes, which are less soluble than achilleine. From all its properties it should undoubtedly be arranged with the bitter extractive substances.

To obtain the acid to which the decoction of the yarrow owes its acid reaction, it was treated with acetate of lead as long as a precipitate resulted, and this suspended in water and decomposed with sulphuretted hydrogen. The liquid obtained was very acid, and still contained some green colouring substance and lime; it was therefore supersaturated with carbonate of potash, which precipitated the lime, and then treated with animal charcoal. The potash-salt was thrown down with acetate of lead, and the precipitate decomposed with sulphuretted hydrogen.

Achilleic acid is not volatile at 212° F.; its solution can therefore be concentrated by evaporation in the water-bath. The greatest concentration to which it can be brought is 1·014825. In this state it is perfectly colourless, but on further evaporation it becomes straw-coloured. Exposed to the air in a glass or porcelain dish, it crystallizes in perfectly colourless four-sided prisms. The crystallized acid requires at 55° F. two parts of cold water for solution; the solution is very acid, blunts the teeth, is void of smell, and strongly reddens blue litmus-paper. Added by drops to a clear solution of acetate of lead, it does not render it in the least turbid; but in a solution of basic acetate of lead it immediately produces a white precipitate, which is very slightly soluble. *Achilleate of potash* is obtained when the acid, diluted with but little water, is poured into a solution of carbonate of potash, so as to neutralize it; the liquid is then filtered, evaporated, and set aside to crystallize. This salt separates in very minute prisms, which can only be seen with a lens;

it has a saline taste, which approaches that of chloride of sodium; in alcohol it is less soluble than in water; exposed to the air it is not altered, but its mother-ley acquires under the same conditions a yellowish tint. *Achilleate of soda* is prepared with carbonate of soda in the same manner as the potash salt. The taste of this salt very much resembles that of the preceding, as also its solubility in water and alcohol, but its crystalline form is very distinct from that of the potash salt; a clear concentrated aqueous solution yielded very beautiful rhombic crystals, which could be discerned with the naked eye. *Achilleate of ammonia* may be prepared by mixing achilleic acid with ammonia; the liquid, when evaporated to a syrup, becomes pale yellow. By exposure to the air for several days it slowly evaporates to a saline mass, which has a similar taste to the potash and soda salt. It is soluble in water and insoluble in pure alcohol. *Achilleate of lime* crystallizes in irregular scales or needles; it is obtained when lime is treated for some hours with slightly diluted achilleic acid, filtered and set aside to crystallize; it is insoluble in absolute alcohol. *Achilleate of magnesia* is difficult to obtain in crystals; when its solution is allowed to evaporate in the air, a yellowish, solid, transparent, gummy mass, which is more soluble in water than in alcohol, is obtained. It is prepared in the same way as the lime salt.

Achilleate of Quinine.—Quinine is dissolved in slightly diluted achilleic acid by allowing the substances to act for several days on one another, stirring them frequently until the liquid no longer reddens litmus-paper. Upon this it is filtered, some alcohol added, heated nearly to boiling, and allowed to cool. Nearly the whole liquid is converted into very beautiful radiately-grouped prismatic crystals. The salt has a very bitter taste, and is easily soluble in water and alcohol. On account of its great solubility, the author suspects that it will be found more adapted for medical purposes than the sulphate of quinine.—Liebig's *Annalen*, lviii. p. 21.

Researches on Coffee. By M. Payen.

The author finds coffee to possess approximatively the following composition:—

Cellulose	34·000
Hygroscopic water	12·000
Fatty substances	10 to 13·000
Glucose, dextrine, and undetermined vegetable acid	15·500
Legumine, caseine (glutine)?	10·000
Chlorogenate of potash and cafeine	3·5 to 5·000
Nitrogenous substance	3·000
Free cafeine	0·800
Concrete essential oil	0·001
Aromatic fluid essential oil	0·002
Mineral substances	6·697
	100·000

According to the analysis of M. Payen, caffeine is represented by the formula $C^8 H^{10} N^2 O^3$. A portion of the caffeine may be obtained directly on treating the coffee at first with æther and then absolute alcohol. On subsequently digesting the coffee with alcohol of 0·912, several substances are taken up, among which is a highly important crystalline body, which contains the remainder of the caffeine in a state of combination. The crystals of this substance are composed of a double salt, resulting from the combination of an organic acid (*chlorogenic acid*) with two bases, caffeine and potash.

When this double salt, which exists naturally in the coffee, is rubbed, after it has been dried at 212°, upon a warm sheet of paper, it becomes electrified to such a degree as to adhere to the blade of a knife in long voluminous flakes. It undergoes no alteration between 212° and 302°; but towards 365° it melts, acquires a beautiful yellow colour, begins to boil, swells so as to occupy five times its volume, and remains spongy, yellow, solid and friable. Heated to 446° it becomes friable, and is in part decomposed; the vapours which are disengaged yield on condensing, acicular crystals of caffeine.

This double chlorogenate of potash and caffeine is scarcely soluble in anhydrous alcohol even when boiling. A saturated boiling solution in alcohol of 0·815 deposits it on cooling in prisms radiating from common centres; it is more soluble in alcohol of 0·848°, from which it also crystallizes more abundantly on cooling; its solubility, in fact, increases with the proportions of water. Pure water dissolves still more, and the aqueous solution, saturated with the assistance of heat, solidifies on cooling. The cold solution, evaporated slowly in a capsule, gradually deposits a mass of minute crystals in warty groups. Even the aqueous solution, on exposure to the air, becomes more or less rapidly changed, and acquires a yellow, and then a greenish-brown colour.

The crystals of the double chlorogenate, heated gently in contact with pure hydrate of potash, acquire a vermilion or orange colour; heated more strongly, the mixture melts, assumes a yellow colour, disengages abundantly ammoniacal vapours, becomes brown, &c. Heated with monohydrated sulphuric acid, the salt developes an intense violet colour, and a bronzed pellicle is formed on its surface; hydrochloric acid produces analogous phænomena, but less distinctly; with nitric acid it exhibits an orange-yellow colour. Acetate of lead yields a pale greenish-yellow flocculent precipitate in aqueous or alcoholic solutions of the chlorogenate; tribasic acetate produces a similar precipitate, but of a pure yellow colour. Nitrate of silver alone causes no alteration; but when it has been previously mixed with a small quantity of ammonia, it produces a yellowish colour with a tint of brown, the liquid becomes turbid, and very soon deposits a pellicle of metallic silver on the sides of the vessel.

To extract the chlorogenic acid, the chlorogenate of lead obtained by one of the three processes above described is decomposed by a current of sulphuretted hydrogen; it yields a solution, which when quickly evaporated leaves a confused mass of crystals of chlorogenic

acid. This acid, purified with small quantities of anhydrous alcohol and dried, is white, soluble in anhydrous alcohol, more soluble in weak alcohol, and very soluble in water, but crystallizes with difficulty. Its aqueous solution, recently saturated at a boiling temperature, crystallizes very slowly in microscopic prisms radiating from common centres, and presenting in the course of 20 to 30 days numerous spherical agglomerations from 1 to 2 millimetres in diameter. Chlorogenic acid dissolved in water has a strong acid reaction; heated in a tube, it melts, becomes yellow, boils, and finally leaves a thin shining layer of charcoal; its vapour is condensed into a brown liquid, which heated rapidly leaves a thin stratum of carbon, which is strongly iridescent. Elementary analysis yielded the following results:—

Carbon	56·0
Hydrogen	5·6
Oxygen	38·4

which leads to the formula $C^{14} H^{8} O^{7}$. The double chlorogenate contains—

Chlorogenic acid	63·5
Potash	7·5
Cafeine	29·0

The cafeine consequently acts the part of a base in the double salt; the new compound exists in the normal state in the perisperm of the fruit of the coffee-tree, from which it can easily be extracted. Among the remarkable properties of chlorogenic acid is the striking power it possesses of developing a very intense green colour, in reference to which it has been named.

Coffee contains some aromatic oils, which the fatty oil obtained by the processes previously described tenaciously retain, and whose properties are modified by the effects of even a very slight roasting. It was precisely in this state that it became important to extract, investigate and weigh these odoriferous bodies. The infusion obtained with hot water, filtered over ground coffee in the proportions of a litre water to 100 grms. of coffee, was distilled in a retort furnished with several successive receivers; after distillation, the first receiver contained a yellowish water, upon which floated some drops of a white concrete essential oil, almost entirely destitute of the agreeable aroma. The second receiver, which had been kept at a temperature of 77° to 86°, contained a liquid upon which floated some traces of a concrete oil which exhaled an agreeable aromatic odour, calling to mind that of the coffee employed, and so intense that a few drops of this water sufficed to communicate to a cup of milk, or of any other liquid void of smell, the agreeable odour of the coffee. The third recipient, cooled several degrees below freezing-point, condensed only a few drops of a liquid, which gave off a mixed odour of the coffee and of empyreumatic hydrocarbons; the same empyreumatic odour prevailed to a greater degree in the gaseous products which escaped from the fourth recipient.

The proportions of the highly volatile empyreumatic hydrocarbon increased more and more the further the roasting of the coffee had been carried beyond that corresponding to a loss in weight of 18 per cent.

Two essential odoriferous oils may be extracted from the aromatic principles by agitating strongly the distilled water containing them with 0·20 of its volume of æther, setting the whole aside for a quarter of an hour, and then removing the supernatant æthereal solution with a pipette. This operation is repeated four times, when on the evaporation of the æther an orange-coloured oil is left, the powerful odour of which calls partly to mind the aroma prevailing more or less in all varieties of coffee. This essential oil is formed of two substances; one, less volatile and less fluid, appears to result from an alteration of the oil possessing the agreeable aromatic odour. The water which has been agitated with æther still contains an æthereal solution of the second volatile oil, possessing a most delicious aromatic odour; its proportions, which are very small in the inferior qualities, but considerable in Mocha coffee, constitute the principal differences between the commercial qualities. The total weight of the oil thus obtained does not amount to more than $\frac{2}{10000}$ths of the weight of the coffee; and this will readily be conceived, as 1 drop of this oil diffuses a strong odour of coffee in a large room.

The variable qualities which have been long noticed in the commercial coffees depend undoubtedly in great part upon the varieties cultivated, and on the habitual or accidental circumstances presented by the soil, exposed position, care employed in the cultivation, manure and atmospheric conditions.

The following are the principal differences between two commercial kinds, respecting the origin of which not the least doubt could be entertained, Mocha coffee and Martinique coffee. Several characters distinguished the Mocha coffee from all the others; the somewhat more abundant fatty matter formed thirteen-hundredths of the total weight; it had a yellowish colour; was very fluid; and it could only be separated into two parts, possessing different melting-points, but difficult to determine. It retained very tenaciously a portion of the aromatic oil, which latter was also more agreeable, and far stronger in comparison.

The fatty substance contained in the coffee of Martinique, extracted by the same method and exhausted with boiling water, is browner and less fluid; it may be separated into four fatty substances, the melting-points of which are respectively 41°, 68°, 122° and 194°. The latter substance resembles the wax of leaves.

The presence of a waxy substance and the green colour of the berries may depend on the period of the harvest, and on the time at which they were shelled. It will be conceived that, on removing the pulp of the fruit when it is filled with juices, the moist perisperm must experience in presence of the air certain reactions, produced by the oxygen; thus the chlorogenate is converted into a green modification, the fatty substances are changed, and the essential oil, secreted in less quantity, may also become changed, and partly escape.

The preceding data allow of explaining the principal effects of the roasting and infusion of coffee. It is most advantageous that the whole mass should be quickly raised to the suitable temperature, that is to say, about 482° F.; under the influence of this temperature, and of the aqueous vapour which is disengaged during the whole of the operation, the double chlorogenate swells up, becomes red, and disaggregates the tissues of the perisperm, setting free a portion of the cafeine which is held in combination. The cellulose, and those substances allied to it, experience a slight caramelization, and yield acid and coloured empyreumatic products. The fatty oils become diffused throughout the mass thus rendered porous, and carry with them the slightly modified essential oils. The fixed and volatile oils therefore are now exposed over great surfaces to the action of the water. If the roasting be discontinued at this period, the berries will have acquired a light chestnut-colour, and will have become sufficiently friable to be readily reduced to powder; on cooling between two capsules, they disengage but a small quantity of vapour, which condenses into a slightly acid water; the loss in weight scarcely exceeds 18 per cent.

If the roasting has been carried further, so that the berries have acquired a more or less dark brown tint, a part will be found to be coated with a violet lustre, which is produced by the chlorogenic acid on its carbonization; a considerable proportion of the empyreumatic hydrocarbons derived from the nitrogenous ingredients and the fatty oils have taken the place of a portion of the aromatic essences disengaged, and during the cooling some drops of these essential oils and of the empyreumatic substances will be condensed on the capsules. The roasted coffee has lost more of its soluble principles the further the roasting has been carried; the useful products have diminished in the proportion of about a fourth; the volatile oil and the aroma likewise decrease in proportion as the torrefaction is increased. If coffee which has been roasted in different degrees is treated with several successive quantities of water, it is found that the first quantity of water best exhausts that coffee which has remained red, that which has become brown less, and still less that which has become chestnut-brown; and as ordinarily the coffee is never entirely exhausted, it is evident that all the advantages are in favour of the coffee slightly roasted.

In the infusion made quickly by a hot filtration and consumed without delay, we especially find the aroma which contributes so powerfully to render the flavour agreeable, and which is particularly due to the most soluble essential oil; a second filtration of hot water may yield a liquid equally coloured, but the aroma of which differing considerably, according to the kind of coffee, characterizes the coarse taste due to the less soluble and less volatile essential oil.—*Journ. de Pharm.*, Oct. 1846.

On the Products of Distillation of Cholesterine.

According to MM. Schwendler and Meissner, when cholesterine is submitted in a retort to dry distillation, it yields a mixture of

products, which condense to a thick tenacious oil; they are not acid, and do not smell of acroleine, and are not dissolved by caustic potash. On distillation with water, an essential oil, having a very agreeable odour resembling that of the geranium, is obtained.—Liebig's *Annalen*, lix. p. 113.

On a Combination of Persulphate of Mercury with Sulphuret of Mercury. *By* Dr. J. Jacobson.

Rose first prepared this compound by treating a solution of persulphate of mercury in sulphuric acid with sulphuretted hydrogen, but did not examine it more closely. Berzelius deduced for it the formula $HgO, SO^3 + HgS$, from the analogous composition of the sulphobasic pernitrate of mercury, Rose having examined this more accurately. To prepare this compound, the author added a clear saturated solution of sulphuretted hydrogen to a clear solution of persulphate of mercury in sulphuric acid until no further precipitate resulted. A portion of the white flocculent precipitate was completely edulcorated with cold water, when it retained its colour unaltered. On drying however at 212°, the surface exhibited a faint, scarcely perceptible, yellowish tint. Another portion of the precipitate was boiled in a platinum dish with distilled water until this was no longer acid towards litmus-paper. After long boiling the white precipitate gradually became yellowish, but yet of a very different colour from that of turpeth; it was then placed on a filter, thoroughly washed with hot water, and dried at 212°, which did not produce any further change of colour. These precipitates, the recent as well as the dried, were somewhat soluble in muriatic, sulphuric and nitric acids, especially with the assistance of heat. When the precipitate was heated with nitric acid, and muriatic acid then added, the action was quick and violent, and the greater portion of the sulphur was converted into sulphuric acid. Hydrate of potash changed the colour even in the cold into a reddish-yellow, and on long boiling into a brownish-red one. Carbonate of soda coloured it yellowish in the cold, and black with the assistance of heat. Both the precipitates which had been treated with water were digested at a gentle heat with nitromuriatic acid until the whole of the sulphuret of mercury was decomposed. The amount of sulphur in the compound was determined as usual, partly from the eliminated sulphur, partly from the precipitate with chloride of barium; the mercury was thrown down by sulphuretted hydrogen, and dried at 212°. The following are the results of the analyses:—

	I. Washed with cold water.	II. Washed with hot water.			
Sulphur.....	8·909	8·99	=	2	8·56
Mercury	79·010	80·87		3	80·80
Oxygen.....	12·081	10·14		5	10·64

The formula $HgS + 2HgO, SO^3$ may be formed for both precipitates. The difference in the amount of mercury and sulphur in

the analyses depends probably on the decomposition not being effected so completely by mere washing with cold water as by continued boiling.—Poggendorff's *Annalen*, lxviii. p. 410.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Analysis of a Venetian Ruby Glass. By J. Böhme.

The powdered glass, which is employed in enamel painting, was decomposed by fusion with soda; a portion digested with muriatic acid; the evaporated mass, after moistening with a few drops of muriatic acid, extracted with water; the silica, with some chloride of lead, collected on a filter; the filtered liquid supersaturated with ammonia, and then digested with hydrosulphate of ammonia. The insoluble metallic sulphurets were collected on a filter, and oxidized with nitric acid, the insoluble residue of sulphate of lead filtered and washed. The solution contained only iron. The liquid filtered from the metallic sulphurets insoluble in the hydrosulphate of ammonia, gave with muriatic acid a bright yellow precipitate of sulphuret of tin and sulphuret of arsenic. The liquid filtered from the metallic sulphurets yielded with oxalic acid and ammonia a precipitate of lime, and with phosphate of soda a slight precipitate of ammonio-phosphate of magnesia. Some gold was extracted, by means of *aqua regia*, from the filtered silica. To determine the alkalies of the glass, it was decomposed with fluoric acid, ignited, exhausted with water, all the other constituents except the alkalies removed, one-half of the liquid treated with chloride of platinum, and the other with antimoniate of potash, by which the presence of potash and soda was proved.

For quantitative analysis, 15·25 grms. of the powdered glass were decomposed by fluoric acid, evaporated to dryness with nitric acid, in order to expel the fluoride of silicium; then, after moistening with a little nitric acid, treated with water and filtered. A small quantity of silica and gold was left on the filter; the latter was extracted with nitromuriatic acid, and precipitated with protochloride of iron. The heavy metals and the lime were removed from the filtered liquid, which was now evaporated, the residue ignited, moistened with muriatic acid, and again ignited until the weight remained constant, and after solution the small quantity of the magnesia contained in it deducted from the weight. The potash in the solution was determined by chloride of platinum, and the soda calculated from the loss. Another quantity of the glass was fused with soda, the silicate decomposed with nitric acid, evaporated to dryness, again moistened with nitric acid and extracted with water. The silica was treated with *aqua regia*, washed and ignited. The lead was precipitated from the solution by sulphate of soda. A third portion of the glass was likewise fused with soda, decomposed with muriatic acid, evaporated and dissolved in water, the silica with some chloride of lead removed, the liquid supersaturated with am-

monia, digested with hydrosulphate of ammonia, and the insoluble metallic sulphurets collected on a filter. These were then oxidized with some sulphuric and nitric acid, evaporated to dryness, and after moistening with some muriatic acid extracted with water; the solution contained only iron, which was determined in the state of peroxide. The liquid filtered from the insoluble metallic sulphurets was supersaturated with muriatic acid, the precipitated sulphuret of tin and sulphuret of arsenic collected on a filter, and the oxide of tin determined. The lime was precipitated from the filtered solution by oxalic acid. The glass contained—

Gold	0·0492
Peroxide of tin	0·6900
Peroxide of iron	2·2000
Oxide of lead	22·9300
Magnesia	0·5000
Lime	3·8000
Soda	5·7960
Potash	6·7000
Silica	58·9800
Arsenic	a trace.
	101·6452

Journ. für Prakt. Chem., xxxviii. p. 333.

On Spurious Spermaceti. By M. Ulex.

This article was imported from New York, under the name of *Solar spermaceti*, in snow-white square blocks of a beautiful radiating fracture. It is hard, friable, not fatty to the touch, and possesses but a slight fatty odour. When 1 part of this substance is heated with 3 parts of alcohol of 0·863, a perfectly clear solution is obtained, which begins to crystallize at 99° F. The principal differences between the solar spermaceti (A) and genuine spermaceti (B) are,—Crystallization,—A, radiate; B, laminar: colour,—A, dull white, slightly yellowish; B, transparent white: spec. grav.,—A, 0·933; B, 0·943: melting-point,—A, 131°; B, 113°. Alcohol of 0·821 dissolves A entirely, but only 3½ per cent. of B. Caustic and carbonated alkalies form soaps with A, not with B. The properties of the solar spermaceti agree essentially with those of margaric acid, which is probably obtained in America by the saponification of pork fat.—*Archiv der Pharm.*, xlvi. p. 292.

Observations on Nicotine, with Description of a Method for determining its Amount in Leaf and Manufactured Tobacco. By M. Schloesing.

The following is the most advantageous method for preparing nicotine:—Tobacco is treated with water, and the solution concentrated; the extract is dissolved in alcohol, which after decantation is likewise concentrated; this last extract is now treated with potash, then agitated with æther, which dissolves the nicotine and also some foreign substances, which are got rid of by precipitating the

alkaloid in the state of oxalate. This precipitate is washed by agitating it with æther, then treated with potash, again dissolved in æther, and submitted to distillation. The residue of the distillation is coloured but limpid, and contains, beside nicotine, water, æther and ammonia; a temperature of 284°, maintained for 12 hours, and assisted by a current of dry hydrogen, suffices to expel these three bodies, so that the nicotine passes pure and colourless, when the temperature is subsequently raised to 356°. 2 lbs. of good tobacco, grown in the department of Lot, is capable of yielding by this process from 50 to 60 grms. of nicotine.

The formula for nicotine. $C^{20}\,H^{14}\,N^2$, proposed by M. Melsens, is confirmed by my analyses; its equivalent, 1012·5, appears however to require doubling, for an equivalent of sulphuric acid neutralizes twice 1012·5; and nicotine is a powerful base, which precipitates the oxides of manganese, iron and silver; it is therefore not very probable that its sulphate, which is neutral towards litmus-paper, is in reality a subsulphate. The above view is also confirmed by the following fact:—If some nicotine is placed in a solution of a salt of lime or baryta, and an excess of carbonic acid passed into the solution, 1 equiv. of carbonate of lime or baryta is precipitated for every 2025 of nicotine.

Nicotine must exist in the tobacco in the state of a salt; for the aqueous, alcoholic and æthereal solutions of this plant behave precisely as if they contained a salt of nicotine. Nicotine absorbs moisture from the atmosphere, but it may be completely deprived of water, æther and ammonia by placing it over mercury in a bell-glass full of hydrogen, by the side of a capsule containing concentrated sulphuric acid.

The amount of nicotine in leaf or manufactured tobacco may be accurately ascertained by a simple and easy process. 10 grms. of tobacco are exhausted with ammoniacal æther in a continuous distillatory apparatus, the ammoniacal gas expelled from the nicotine solution by boiling, then decanted, and, after evaporation of the æther, neutralized with a solution of sulphuric acid of known strength. This process will be applicable, with some slight modifications, to most of the organic alkalies. Its accuracy was proved by ascertaining,—1st, that the displacement of the nicotine by ammonia and the exhaustion by the æther are perfect; 2nd, that merely boiling the solution of nicotine suffices to expel the ammoniacal gas dissolved; 3rd, that during this boiling no nicotine is lost; 4th, that a proportionality is found between different weights of nicotine, and the quantities of normal liquid required for their neutralization; 5th, that there is no other substance besides the nicotine capable of absorbing the acid; 6th, that if the tobacco contained any other bases than nicotine, they would not interfere; lastly, nearly the whole of the nicotine contained in 10 grms. of Lot tobacco was extracted, purified, weighed and analysed; the weight was 0·766, and should have been, according to the test with the normal solution, 0·796.

The following amounts of nicotine were indicated by testing in this manner various French and American tobaccos:—

Lot	7·96 per cent of the dried tobacco.			
Lot et Garonne	7·34	...	...	...
Nord	6·58	...	...	...
Ile et Vilaine	6·29	...	...	...
Pas de Calais	4·94	...	...	...
Alsatia.....	3·21	...	...	...
Virginia	6·87	...	...	...
Kentucky.....	6·09	...	...	...
Maryland.....	2·29	...	...	...
Havannah less than..	2·00	...	...	...

It will be seen from this table that those tobaccos which contain the most nicotine are also the best suited for the manufacture of snuff.

The above method of determining the amount of nicotine applied to snuff indicated as a mean 2·04 nicotine per cent. of the dried powder; whence it is concluded that about two-thirds of the nicotine contained in the mixed leaves destined for the manufacture of snuff is destroyed by the fermentation. The ammonia exists in the snuff in the state of a salt; the nicotine, partly in a free state, and partly as a neutral salt, or altogether in the state of a subsalt. It is to these two salts that snuff owes its property of exciting the mucous membrane of the nose.

This memoir is the first part of an investigation on the composition of tobacco leaves and on the fermentation of tobacco, begun in the laboratory of the *Manufacture des Tabacs*, under the direction of M. Fremy.—*Comptes Rendus*, Dec. 21, 1846.

Analysis of a Powder employed for cleaning Silver Plate.
By M. Louyet.

This powder was sent to me for analysis by a jeweller, who suspected it to contain mercury; it was of a rose colour, soft to the touch, and of a chalky aspect; it had moreover a calcareous smell, effervesced lively when treated with hydrochloric acid, but did not dissolve entirely in an excess of this acid even on the application of heat. The residue had the appearance of silica, and was of a violet red colour. 6·3 grms. of this powder yielded on analysis—

	grms.
Carbonate of lead	0·816
Carbonate of lime	3·330
Carbonate of magnesia	0·318
Alumina	0·840
Silica	0·500
Peroxide of iron.....	0·330
Loss.....	0·166

This powder gives a most beautiful lustre to plate and objects of jewellery.—*Bulletin du Musée de l'Industrie*, 1846.

Adulteration of Soap.

Dr. Riegel found, on dissolving an apparently very beautiful but at the same time very cheap soap in spirit, a considerable quantity of animal gelatine, which of late years has frequently occurred in the Spanish or Venetian soap. The soap contained 41 per cent. animal gelatine, 26 per cent. soda soap, and 33 per cent. water.—*Jahrb. für Prakt. Pharm.*, xii. p. 296.

REVIEW.

On the Pathology and Treatment of Scrofula; being the Fothergillian Prize Essay for 1846. *By* R. M. Glover, M.D., &c. London, Churchill.

This work, as implied in the title, gained the Fothergillian prize for 1846, offered by the Medical Society of London, and is, we think, well-entitled to such reward.

The study of disease has materially changed its aspect within the last few years, and will in all probability be completely altered in a few years more, owing to the extensive application of the collateral sciences to its investigation. The dependence of the functions of the body, or at least a large number of them, upon physical and chemical laws, is now becoming daily more evident to those who are sufficiently interested in the science of their profession to scrutinize the operations of nature, or to peruse the results of others who are engaged in such investigations.

The disease of which the present work treats is one of the greatest importance to mankind, inasmuch as it is fearfully common and destructive under a great variety of forms; it is also perhaps among the last whose pathology will be well understood, inasmuch as it involves so large a number of the tissues and fluids of the body. The author has, with great industry, not only collected the most important historical facts concerning it, but has appended many valuable observations of his own, which may probably throw considerable light upon the action of some medicines. The most important fluids of the body, and the morbid productions, have been analysed at his own hands; this is what we think all practical men may and ought to be able to do. We cannot adduce a more important proof of the necessity of some share of chemical knowledge to a practical physician than the absurdity of M. Lugol, who uses iodine baths with great benefit in these cases, taking care, however, from an ignorance of chemical principles, that the iodine is volatilized and expelled from the fluid before the patient is immersed in it! Such doings as this are common amongst a large number of "routine" practitioners, who continue in the track of their forefathers, and probably if they lived for centuries would remain in *statu quo*, with the exception of being more firmly impressed with their doctrines from mere habit.

The most important morbid product evolved in scrofulous patients is tubercle; its nature and composition are still not satisfactorily made out. The excellent analyses made by Scherer not being usually known, we shall annex an example of them from our author's work, at the same time giving one or two of those by the author himself. We hardly know at present whether the composition of tubercle is constant and uniform at the same stages of development, and whether the differences found on analysis depend upon the remains of admixed partly disorganized tissues and blood-vessels or not; it is impossible perfectly to separate them from it.

Scherer rubbed the tuberculated glands from the belly of a scrofulous child with water; the filtered fluid was precipitated by nitric acid, but not by cold acetic acid nor alum; the former reagent however gave a precipitate in the heated fluid. Hence he inferred the existence of albuminate of soda, and the absence of caseine and of pyine (which our readers will recollect Mulder has shown to consist of tritoxide of proteine). The residue on the filter was exhausted of soluble albumen by a solution of nitrate of potash, and subsequently boiled with water, spirit, alcohol and æther. The aqueous decoction yielded traces of pyine with acetic acid and alum. The spirituous decoction contained yellowish extractive matter, and the alcoholic and ætherial solutions much fat, especially elaine.

The mass, fresh from the body, when dried in the water-bath, yielded—

Water	77·678
Solids	22·322

On incineration he obtained 0·526 per cent. of ash, consisting of a little chloride of sodium, much carbonate with some sulphate and phosphate of soda, and a very little phosphate of lime. The mass, when freed from all extractive matters, yielded—

Carbon	54·125
Hydrogen	7·281
Nitrogen	15·892—16·086
Oxygen	22·702

Dr. Glover found mesenteric tubercle from a phthisical patient to consist of—

Water	80·3
Solids	19·7

It was treated with the same solvents as in Scherer's analysis; the aqueous extract contained mucous matter, insoluble in boiling water; the filtered solution gave precipitates with acetic acid and alum insoluble in excess; it also contained an extractive matter and a large amount of fat. The residual proteine compound yielded 1·37 per cent. ash; and on ultimate analysis—

Carbon	54·97
Hydrogen	6·63
Nitrogen	12·31
Oxygen	26·09

The small quantity of nitrogen thus obtained is worthy of remark, compared with the results of Scherer.

In a specimen of crude mesenteric tubercle the author found—

Water	81·25
Solids	18·75

The residual proteine compound gave 2·5 per cent. of ash, and it yielded 56·40 per cent. carbon and 15·56 per cent. nitrogen.

The proximate composition of 37·50 grms. of the entire mass was—

Fat		6·75
Extractive, soluble in spirit and water, and loss		7·50
Salts	Chlorides	0·45
	Earthy phosphates	0·58
	Alkaline salts	0·50
Proteine residue		21·72

The following results were obtained in the organic analysis of the proteine basis of a mass of crude tubercle of the lung, after the usual removal of the extractives:—

	Scherer.	Glover.
Carbon	53·884	53·43
Hydrogen	7·112	6·64
Nitrogen	17·237	14·02
Oxygen	21·767	25·91

Our limited space prevents us from abstracting several other interesting analyses, for the perusal of which we must refer the reader to the original, in which several are detailed of the blood, urine, &c., as modified by disease and by the exhibition of medicines. We are also obliged to pass over, as foreign to our pages, some interesting remarks on the etiology and treatment of scrofula.

The following speculations on the action of iodine are too interesting to be omitted:—"When we consider the probable connexion of the secondary digestion of the tissues of which the principles of the urine are the chief results, with the state of the blood and the respiration, we may understand the important part which the use of a remedy like iodine may play in the treatment of such a disease as scrofula,—1st, in quickening the power of absorption and getting rid of the effused albumen, where this is not in such a form as to preclude all action of the kind; and 2nd, in removing the excess of albuminous substance in the blood. Again, we deem it by no means an improbable supposition, that the chief seat of the formation of urea may be in the lymphatic glands of the general system. This substance is not formed in the kidneys, as we know by the experiments of Prevost and Dumas. Now, is it not very probable that the lymphatic glands may play such a part on fluids absorbed from the digestion of the tissues, as there is reason to attribute to those of the mesentery and others, in the course of the chyle, upon this fluid?" The latter idea however is not new.

In conclusion, we may strongly recommend a perusal of this work

to such as are interested in the pathology and treatment of this destructive disease; in it they will find a complete exposition of the present state of our knowledge of the malady, together with many valuable results of the author's experience in the use of remedies which are but little known or used, and much interesting matter elucidating the chemical pathology of the disease.

PATENT.

Patent granted to Isaac Hawker Bedford, Birmingham, *for Improvements in the Manufacture of Window and other Glass.*

This invention consists, first, in certain improvements in staining sheet glass, and vessels and other articles made of glass; and secondly, in improvements in etching sheet-glass, and vessels and other articles made of glass. That part of the invention which relates to staining glass has for its object the use of copper in staining articles made of glass, so as to produce a red colour. The sheet-glass, and vessels or other articles of glass, are to be made in the usual way; and when articles of cut glass are to be stained, they may be stained before or after cutting and polishing, and the staining may cover the whole, or any part or parts of the surface. It should however be remarked, that this part of the invention is performed most successfully with those descriptions of glass which are made without the use of soda. The articles of glass being made, and their surfaces well cleaned, they are treated in the following manner:—1 part by weight of sulphuret of copper, 2 parts of the scales of iron obtained from a smith's forge, 3 parts of sulphate of copper burned to whiteness, and 4 parts of calcined yellow ochre, are ground as finely as possible with the essence of turpentine; and it is advisable to mix with such turpentine a small quantity of the essence of turpentine that has become rather thick by long exposure to the atmosphere, which prevents the mixture chipping off after becoming dry on the glass. The mixture thus produced is of the consistency of cream, and is laid on the surface of the glass with a brush, and allowed to dry. The articles of glass are then placed in an ordinary stainer's muffle, and heated to as high a degree of heat as the glass can be subjected to without melting; after which the fire is drawn off, and the articles of glass are allowed to cool down slowly. When cold, the articles are to be washed; and then, on looking in a direction edgewise of the glass, it should present a greenish-yellow appearance if lead has been used in the making of the glass. The colour obtained will differ according to the composition of the glass. The articles of glass are again placed in a muffle, and again heated to the degree above mentioned; then the fire is withdrawn, and a quantity of small coal is introduced into the lower part of the muffle; for this purpose it is convenient to have

the cover of the muffle in two parts, so that a small part of the cover at the lower part of the muffle may be removed to allow of a shallow tray being slid into the muffle under the articles of glass placed on the perforated shelves above. The quantity of coal introduced into a muffle 24 inches in diameter and 30 inches in length, is 4 lbs.; and then the muffle is completely closed and luted, by which means the products of the coal are prevented from escaping. The muffle and the articles of glass are allowed to cool down, and when cold the articles of glass are taken out; and they will generally be found to offer a brownish-red colour on looking through them. The articles that exhibit this colour are then to be placed in another muffle (which has been lime-washed), and again heated up to the same degree of heat as before mentioned; the fire is to be removed, and the muffle and the articles of glass cooled down; and when cold the articles of glass should present the red colour desired.

It should be stated that a red colour of the depth and tone desired is not at all times obtained by going once through the process above explained, in which cases the articles are again and again to be subjected to the same processes. A workman will, however, with care, after some experience, be able to judge whether the effect desired has been obtained by each part of the process; and if not, he will not carry such articles through the remainder of the process, but will repeat the previous part or parts of the process till the appearance desired has been obtained. The patentee does not confine himself to the exact details of the above process, so long as copper is used when staining articles made of glass so as to obtain a red colour.

In carrying out the second part of the invention, which has for its object the ornamenting of glass by a peculiar process of etching, the patentee grinds 5 parts of puce-coloured oxide of lead (peroxide) and 1 part of flux (the flux employed consisting of 17 parts glass of borax and 13 parts red lead fused together) with turpentine; and with this composition the artist paints the desired devices or designs upon the surface of glass to be etched. When coloured glass is to be etched, the patentee prefers to use acetate of lead in place of the oxide of lead above mentioned. The articles are then allowed to dry, and are fired in the same manner as when gilding on glass; after which the articles are permitted to cool, and when cold they are dipped in a weak solution of nitric acid in water; and so soon as the painted designs are acted on, the articles are placed in water and the surfaces cleansed by rubbing off the preparation above mentioned. The patentee does not confine himself to the exact details of the above process, so long as lead is used and removed by acid.—Sealed Dec. 12, 1845.

THE CHEMICAL GAZETTE.

No. CIII.—February 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches upon the Hydrates. By E. Fremy.

It is barely necessary to mention the number of theories which have been proposed at various periods to explain the part which the water acts in saline combinations; some chemists have regarded the hydrated acids as true hydracids; others have assimilated them to salts in which the water acts the part of a base. Some admit that it is the water which imparts to the anhydrous acids the property of combining with bases; others compare the hydrated acids to oxygen compounds in which the equivalents of oxygen are replaced by hydrogen, &c.

My object is not to discuss in this place all these hypotheses, which are frequently sustained with great ingenuity by their authors, but merely to show that in this important question the opinions of chemists are much divided. To remove the doubts which prevail respecting the theory of the hydrates, I have considered it indispensable to resume completely the investigation of the compounds which acids, bases and salts are capable of forming with water.

Every chemist is aware that there appears to exist in several cases a certain relation between the capacity of saturation of an acid and the quantity of water which this acid retains when it is hydrated. This fact has been placed beyond all doubt by Mr. Graham in his investigation on phosphoric acid; and I believe I have likewise established it for the organic acids in my researches on the tartaric and paratartaric acids. I have shown that the capacity of saturation of these acids decreased in proportion as they became dehydrated; but must we admit, in a general manner, that all acids which have become anhydrous have lost the property of combining with bases, and should no longer be considered as acids? It is this question, so important in reference to the statics of chemistry, which it appeared first of all interesting to examine.

The property which acids possess of combining with bases in order to saturate them, and of displacing other acids from their saline combinations according to the principles of Berthollet, must be considered as their essential character. I have, therefore, in

order to determine the acidity of the anhydrous acids, caused them to act upon anhydrous bases, or upon salts containing acids of a less fixed nature. I have submitted to this double test nearly all the anhydrous acids known, as the carbonic, sulphurous, sulphuric, phosphoric, silicic, boracic, stannic, &c. These experiments partly confirm facts which are already known, and prove that the above acids may present all the characters of acids without the intervention of water. As an example of these reactions, I may state that carefully dried sulphurous acid completely decomposes dry carbonate of soda at a gentle heat, and forms sulphite of soda, which in its turn may be decomposed by an anhydrous acid of a more fixed nature than the sulphurous. There exists therefore a certain number of acids which preserve their acid reaction even when they become anhydrous. This point first established, I wished to ascertain whether all the acids were capable of forming anhydrous salts with bases, and whether there did not exist a certain number of salts in which water was an indispensable element.

It is generally admitted that the water of crystallization contained in the salt is outside of the saline molecule, and that it only has influence upon some of the physical properties of the salt. Recent experiments, however, seem to prove that in many cases the water appears to be indispensable to the constitution of the salt. M. Wurtz has proved that the phosphites and the hypophosphites all contain a certain quantity of water, of which they cannot be deprived without experiencing entire decomposition. I shall show that these hydrates are far more numerous than is generally suspected, and that several classes of salts exist, the molecules of which are truly ternary, and are always formed by the combination of an acid, a base and water. But I shall first call to mind that M. Regnault has long considered the water of crystallization as forming with the anhydrous salts, groups which cannot be modified without at the same time producing a considerable change in the properties of the salts; and that Chevreul has always arranged in different species the salts formed by the same acid and the same base, but which contain different proportions of water. This view is fully confirmed by my experiments.

I imagined that if the powerful acids, such as the sulphuric, nitric, &c., form with equally powerful bases salts which are almost constantly anhydrous, this would not be the case with those acids which possess but a weak affinity for bases. My attention was therefore directed to those hydrates of the metallic oxides which are soluble in alkalies, and which may be regarded as weak acids; I found that these bodies have the property of entering into combination with bases only in the state of hydrates. Thus the hydrate of the binoxide of copper, dried at the ordinary temperature in dry air, is represented by the formula CuO 2HO. In this state it is entirely soluble in an excess of potash and soda; the solution is of a beautiful blue; when evaporated even *in vacuo*, it is decomposed, and deposits anhydrous oxide of copper, which is insoluble in the alkalies.

The hydrates of the oxides of tin, antimony and chromium are represented, according to my analyses, by the formulæ

$$SnO, HO; SbO^3, HO; Cr^2 O^3, 10HO.$$

They dissolve in alkalies, and become insoluble on losing their water. I have convinced myself that the insolubility of these oxides in alkalies is really due to the elimination of a certain quantity of water, and not to those isomeric modifications which certain oxides experience when they are calcined. I found it quite impossible to obtain crystalline combinations of the preceding hydrates with the alkalies, for on evaporation even *in vacuo* the excess of the alkali, which it is requisite to employ, seizes the water of the hydrates, or, acting perhaps merely by its presence, determines the precipitation of the anhydrous oxides. Nevertheless the preceding combinations prove that the existence of certain saline groups is only possible with the participation of water; they show that various hydrates owe their solubility in the alkalies solely to their hydrate water.

The investigation of the stannic and antimonic acids furnished me with striking examples of hydrates, which, similar to the preceding, combine with bases, retaining their constitutional water, but which, on account of their stability, form hydrated salts, which cannot easily be isolated. I think I have proved, in a preceding memoir, that the opinion of Berzelius respecting the two stannic acids can no longer be admitted, and that they possess different equivalents. The new facts detailed in this paper confirm my former experiments; they establish marked differences between stannic acid and that which I have called the *metastannic*. In fact, it results from my recent analyses that metastannic acid is capable of forming three hydrates with water:—the first is insoluble in nitric acid and soluble in ammonia, and is obtained by precipitating a metastannate with an acid; the second is produced by the action of nitric acid upon tin; its formula is $Sn^5 O^{10}, 10HO$; it is insoluble in ammonia and nitric acid; the third is obtained by drying the preceding hydrate at 260°; its formula is $Sn^5 O^{10}, 4HO$. But it is especially in its combinations with bases that metastannic acid offers peculiar interest, differing widely from stannic acid. I have proved, in fact, by numerous analyses, that the neutral metastannates formed in the presence of a large excess of alkali are represented by the general formula $Sn^5 O^{10}, MO, 4HO$, while the stannates are represented by SnO^2, MO; the equivalent of metastannic acid is therefore five times higher than that of stannic acid. I have moreover established by experiments, which to me appear decisive, that the metastannates are always hydrated, that they are necessarily ternary, and are decomposed when deprived of their water; in this case the metastannic acid has lost its acidity, while the stannates may be reduced, like almost all other salts, to the anhydrous state without being decomposed.

That the water is essential to the constitution of the metastannates may be readily proved by the following experiments:—When the metastannate of potash is heated slightly, so as to remove its water of combination, the separation of the acid and base is immediately produced; on treating the dehydrated salt with water,

nothing is dissolved but potash, which does not retain a trace of metastannic acid. Here we have a decomposition effected upon a well-defined salt similar to that which a solution of the binoxide of copper in potash experiences when heated. The dehydration of the metastannate of soda is perhaps still more remarkable, for it takes place below 212°. This salt is soluble in cold water; but if thrown into boiling water, it is instantly decomposed, and the water contains only pure soda. I think this fact important, that the same oxide is able, by combining with different proportions of water, to form two acids, which are distinguished from one another by their properties, their equivalent, and their mode of combination with bases. I shall subsequently show that this fact is not isolated.

I shall now present a summary of the experiments to which I have recently submitted antimonic acid and the antimoniates. I first sought to ascertain whether antimonic acid might not, like stannic acid, combine with water in several proportions; with this view I compared the hydrates obtained by the decomposition of the perchloride of antimony in water, and the precipitation of an antimoniate by an acid. From my researches it results, that antimonic acid, prepared by different methods, and desiccated in dry air, exhibits a constant composition, corresponding to the formula SbO^5, 4HO. The characters of this acid remain invariable in whatever way it is prepared. Everything tends to show that there exists but one hydrate of antimonic acid, or at least that the other hydrates cannot be easily isolated.

If the hydrate of antimonic acid does not offer much interest, it is otherwise with the combinations of the antimoniates with water. I found, for instance, that each antimoniate could combine with water in several proportions, and form ternary groups, a kind of double salts, which cannot be compared to the ordinary hydrated salts, for each group possesses special chemical reactions, which differ in proportion as the salt loses its water. Thus antimonic acid forms with potash a neutral anhydrous salt, which is represented by the formula $SbO^5 KO$. This salt is perfectly insoluble in water, and only becomes soluble by long boiling; it is this antimoniate which is produced when antimony is acted upon by nitre, and which has generally been considered to be an acid antimoniate.

This salt combines with water in two different proportions. One of these compounds contains 7 equivs. water; it crystallizes, and its principal character is that of forming in salts of soda a crystalline precipitate which is almost insoluble in water. By boiling for a few minutes the crystallized antimoniate of potash is further hydrated, and converted into a gummy salt which has lost the property of precipitating the salts of soda; but when it is gently dried, it is slowly dehydrated, passing through the intermediate stages I have described, and reconverted into the anhydrous modification of antimoniate of potash, which is insoluble in water.

Each antimoniate can, like the salt of potash, form two series of hydrates with water, which exhibit common generic characters. Thus the antimoniate of ammonia, which I have examined with the

greatest care, combines with water in two proportions, like the salt of potash. One of these hydrates is represented by the formula $SbO^5, NH^3, HO + 6HO$; it is crystalline, and precipitates soda salts. The other contains 1 equiv. of water less than the preceding, and is perfectly insoluble in water. The slightest influences, as a gentle elevation of temperature or the action of light, frequently suffice to determine the elimination of 1 equiv. water in the crystalline antimoniate of ammonia, and to convert it into an insoluble powder.—*Comptes Rendus*, Dec. 21, 1846.

On the Composition of Quinoidine. By J. Liebig.

As is well known, Serturner regarded quinoidine as a peculiar base which accompanies quinine and cinchonine in the red and yellow species of *Cinchona*. According to Henry and Delondre, and likewise Geiger, quinoidine consists of quinine and cinchonine, accompanied by a resinous substance, which prevents the two bases from crystallizing. Liebig found, on distilling some ounces of quinoidine with strong solution of potash, that it yielded quite as much quinoleine as pure quinine. It is quite evident that quinoidine contains no resin, but consists altogether of an organic alkali, since, on being warmed with sulphate of copper, it dissolves entirely, separating oxide of copper. Mere traces of quinine and cinchonine could be detected in it. For analysis, quinoidine obtained from the æthereal solution, or the precipitate obtained by an alkali from the solution of the crude quinoidine in sulphate of copper, after removal of the copper by sulphuretted hydrogen, were employed. The following numbers were obtained:—

Carbon	73·49	73·14	74·33
Hydrogen	7·69	7·64	7·57
Nitrogen	8·79	8·79	8·79

The double salt of platinum, which is obtained from the muriatic solution with chloride of platinum, perfectly resembles the double salt of quinine, and yielded—

Carbon	32·44		
Hydrogen	3·86		
Platinum	26·33	26·32	26·45

It is evident, therefore, that quinoidine and quinine possess the same composition and the same atomic weight, and differ only in form, the one being crystalline while the other is amorphous.—Liebig's *Annalen*, lviii. p. 348.

On the Occurrence of Arsenic in Mineral Waters.

Some time ago M. Tripier detected the presence of arsenic in the mineral water of Meskoutine in Algiers. Walchner has found that small quantities of copper and arsenic always accompany iron, and frequently in such quantity that they influence the quality of the iron obtained from the ores. To detect the metals in the iron ores,

Walchner dissolved them in muriatic acid, and passed a current of sulphuretted hydrogen through the liquid until the latter was perfectly saturated with it, and smelled still strongly of it after some hours. The precipitate thus obtained was submitted to the ordinary tests for copper and arsenic. As the native hydrated oxide of iron, sparry iron ore, and the oolitic and lenticular iron ores of the Jura formation, which may be regarded as the deposits of ferruginous springs, as well as bog iron ore, contain copper and arsenic, the author endeavoured to detect these metals in the sediments of chalybeate waters. The sediments were treated in the manner above described, the sulphuretted hydrogen prepared from perfectly pure sulphuret of iron or sulphuret of calcium, and previously well washed. The author examined in this manner the sediments of the chalybeate waters of Griesbach, Rippoldsau, Teinach, Rothenfels and Cannstadt, as also the hot springs of Wiesbaden and the effervescent waters of Ems, Pyrmont, Lamscheid, and Brohl near Andernach; and found arsenic and copper in all of them, and moreover antimony in that of Wiesbaden, but always, as might be expected, in very minute quantities. The reason why these metals have been overlooked in the previous analyses of these mineral waters is owing to their not having been sought for, and the quantities of water employed for the experiments not being sufficiently large. The author previously examined several ferruginous soils for these two metals, for instance those of Wiesloch and Nussloch near Heidelberg, which are cultivated with vines and field fruits; and these, and several others, led to the same result. M. Walchner, moreover, detected both these metals in the meteorites discovered by Pallas, in that of Yuanhuitlan near Oaxaca, in that of Tennessee, and in the meteoric iron contained in the collection of Yale College, Connecticut.

Flandin, who, in consequence of the observations of Walchner, examined the chalybeate water of Passy near Paris, and employed $6\frac{1}{2}$ litres for the purpose, could not detect any trace of copper or arsenic in it. Figuier, on the other hand, who examined the residue obtained by the spontaneous evaporation of the water of Wiesbaden, arrived at the same results as Walchner. As muriatic acid is difficult to free from arsenic, M. Figuier employed a perfectly pure sulphuric acid. 100 grms. of the above residue were boiled with sulphuric acid until the oxide of iron had entirely dissolved; the insoluble sulphate of lime was separated by filtration, and the solution supersaturated with pure potash, in order to throw down the excess of peroxide of iron and protoxide of manganese, but to hold in solution the arsenite and arseniate of iron. The arsenic must necessarily be contained in the alkaline liquid; this therefore was treated with an excess of sulphuric acid, and placed in Marsh's apparatus, when metallic arsenic was distinctly obtained. The solution of the metallic ring in nitric acid yielded with nitrate of silver and with sulphuretted hydrogen the characteristic precipitates of arsenic. In order to demonstrate the presence of arsenic in some other manner, M. Figuier dissolved the residue of the mineral water in muriatic acid, and passed sulphuretted hydrogen through the solution, after it

had been first washed with water, and then through a bottle filled with the muriatic acid which had been employed for dissolving the residue, in order to prove the absence of arsenic in the muriatic acid. A distinct yellow precipitate very soon made its appearance in the solution of the residue, while the muriatic acid only became slightly turbid after some time, owing to the elimination of sulphur. The above precipitate was dissolved in ammonia; the solution filtered, precipitated with muriatic acid, and dissolved in *aqua regia*, when the characteristic reactions of arsenic were obtained with the solution of the concentrated residue. Figuier is inclined to believe that the arsenic, respecting the presence of which in the mineral water of Wiesbaden not the least doubt can any longer prevail, is contained in it in the form of arsenite of soda. When the protoxide of iron contained in the water is further oxidized, it combines with the arsenious acid, and is deposited as arsenite of iron. 1 litre of water from the hot spring in Wiesbaden left 0·557 grm. residue insoluble in boiling water. 200 grm. of the latter represent therefore about 359 litres of water, and contain 0·124 grm. metallic arsenic = 0·163 grm. arsenious acid. 100 litres of water consequently contain about 0·045 grm. arsenious acid. The usual dose of *Liquor arsenicalis Boudin* prescribed for sick persons contains 0·005 grm. arsenious acid, consequently just as much as 11 litres of the Wiesbaden water.—*Comptes Rendus*, xxiii. pp. 612–634; and *Gaz. Médic. de Paris*, No. xliv. p. 847.

On the Composition of Pyroxyline. *By* J. Pelouze.

Before noticing the results of the analyses, I shall draw attention to an important point, the study of which may serve to throw much light on the composition of this inflammable substance, viz. the proportion of pyroxyline which purified cotton is capable of yielding. It appears to be well established that the only substances which result from the action of concentrated nitric acid upon cellulose are water and pyroxyline. In fact, no gas is disengaged in this remarkable reaction; the acid liquid, saturated with ammonia, evaporated and decomposed by heat, leaves no residue, and does not afford any or only mere traces of carbonic acid; on the other hand, it decreases in strength, becoming more hydrated, and very soon unsuited for the preparation of any further quantity of inflammable substance. The sulphuric acid, although highly important as respects its œconomic manufacture, produces no alteration in this state of things. The cotton itself scarcely changes in appearance, and its conversion into pyroxyline is instantaneous.

Purified cotton and Swedish filtering paper, dried between 300° F. and 320°, and immersed in a mixture of monohydrated nitric and sulphuric acids, yield 175 parts of pyroxyline for every 100 parts of pure cellulose. This pyroxyline, before being weighed, was dried between 104° and 130°, at which temperature it is not altered in a perceptible manner; but at a higher temperature, approaching 212°, it diffuses a very decided odour of nitric acid, and is slowly decom-

posed. In the space of an hour, between 212° and 220°, it has sometimes lost 10 per cent. in weight, becomes yellow, very friable, and frequently takes fire suddenly.

The cotton, after an immersion of some minutes, is entirely converted into pyroxyline. I have ascertained that it is not increased in weight by a second immersion in the monohydrated acids; on the contrary, a very small quantity is destroyed or dissolved, which is precipitated by water in the form of light flakes.

As observed by M. Richier, pyroxyline is entirely soluble in the acetic æthers of alcohol and of wood-spirit; this property enables us to obtain the pyroxyline in powder; for this purpose it is merely requisite to expose it for a few instants to the action of a small quantity of one or the other of these æthers, and to rub it gently between the fingers or in a mortar. This property has also enabled me to ascertain the purity of the pyroxyline before submitting it to analysis. The solution of gun-cotton in dilute sulphuric acid at a lower temperature than 212°, without imparting any colour to the liquid, as pointed out by M. Vankercknoff, has likewise enabled me to ascertain the absence of cellulose in pyroxyline.

With the aid of these characters I have been able to proceed in a more satisfactory manner with the analysis of pyroxyline; to which I have devoted the greater care and attention, as the numbers which I formerly obtained differed considerably from those deduced from the formula assigned to pyroxyline by M. Peligot. The constancy of the results of my analyses; their number, which is considerable; the harmony which they exhibit with the metamorphoses of cellulose into pyroxyline; the combustion of this substance, effected in the most simple manner, like that of other organic substances—all these circumstances justify me in regarding as accurate the composition which I have found for the nitrate of cellulose, viz.—

	Minimum.	Maximum.		
Carbon	25·2	25·8	24	25·40
Hydrogen	2·9	3·2	17	2·99
Nitrogen	12·6	13·0	5	12·34
Oxygen	..	..	42	59·27

This composition supposes that 100 parts of pure dry cotton should yield 174·9 pyroxyline, and I found from 174 to 176.

With a view to check the preceding analyses, and also to ascertain the purity of the substances employed in the preparation of pyroxyline, I determined the composition of cellulose on portions of the same specimens that were to be converted into inflammable substance. I found, for cotton purified as above described and dried at 320°, the composition long since assigned to it by M. Payen, *i. e.* $C^{12} H^{10} O^{10}$. This formula, however, should be doubled, in order to represent 1 equiv. of cellulose, when the conversion of this substance into pyroxyline would take place according to the following equation:—

$$\underbrace{C^{24} H^{20} O^{20}}_{\text{1 equiv. cellulose.}} + 5(NO^5, HO) = 8HO + \underbrace{C^{24} H^{17} O^{17}, 5NO^5}_{\text{1 equiv. pyroxyline.}}.$$

5 equivs. of nitric acid, in acting upon 1 equiv. of cellulose, would give rise to 8 equivs. of water and 1 equiv. of pyroxyline; of these 8 equivs. of water, 3 would be furnished by the organic substance and 5 from the monohydrated nitric acid. This elimination of so considerable a quantity of water explains why a mixture of concentrated nitric and sulphuric acids rapidly weakens when cotton is immersed in it.

The formula for pyroxyline, $C^{24}H^{17}O^{17},5NO^5$, explains why this explosive substance leaves no carbonaceous residue on its deflagration. It is seen, in fact, that its complete transformation into elastic fluids and aqueous vapour is possible; for it contains, independently of the nitrogen and of the elements of water, 24 equivs. carbon to 25 equivs. oxygen, *i. e.* a more than sufficient proportion of this last body to convert the whole of its carbon into carbonic oxide.

The products of the detonation of pyroxyline may be represented as follows:—

46 vols. of carbonic oxide	$C^{23}O^{25}$
2 vols. of carbonic acid.....	CO^2
10 vols. of nitrogen.....	$5N$
34 vols. of aqueous vapour.....	$17HO$

the sum of which represents 1 equiv. of pyroxyline, $C^{24}H^{17}O^{17},5NO^5$. However, these numbers are purely theoretical, and must necessarily be altered or modified by a number of circumstances, among which may be mentioned the more or less elevated pressures or temperatures under which the detonation of the pyroxyline may occur.—*Comptes Rendus*, Jan. 4, 1847.

Observations on Pyroxyline. *By* P. J. Vankercknoff.

When pyroxyline and ordinary cotton are treated with concentrated sulphuric acid, they both dissolve in the cold, the cotton however much easier than the pyroxyline. When these solutions are heated they behave differently; that of the cotton soon becomes highly coloured, as is well known, while that of the pyroxyline produces at first a considerable disengagement of gas, and only becomes subsequently coloured. If, instead of using concentrated sulphuric acid, we take that having a density of 1·70 or 1·68, the two substances are still observed to dissolve entirely in the cold, but not the least colorization of the solution of the pyroxyline is observed when the temperature does not exceed 212°. An acid of still lower density, for instance of 1·46, produces the same effects, but more slowly. I propose, therefore, as a very simple method of distinguishing pyroxyline from cotton, and also of judging of the purity of the first of these bodies, treating the substance in question with sulphuric acid of 1·50–1·70, and subsequently heating in the water-bath; a more or less decided colouring indicates the presence of cotton even before the bath has acquired a temperature of 196° F., while pyroxyline merely disengages gas without imparting any colour to the liquid. I have frequently heated the solution of pure pyroxyline in the water-bath for

more than an hour, without the acid having acquired the slightest tint of brown or black. The method is, moreover, equally applicable to pyroxyline obtained from other substances than cotton, provided it is completely pure, which appears to me in many cases to be somewhat difficult to attain.

Among the gases liberated during the treatment of pyroxyline with sulphuric acid, we meet with carbonic acid and deutoxide of nitrogen; an organic substance, containing but little carbon, appears to remain in solution; for when the temperature exceeds 212° or the acid is boiled, a colouring is observed. I do not know whether it will be possible to expel, by means of sulphuric acid, the nitrogen acid (whichever it be) which is contained in the pyroxyline in combination with an organic substance, and to set this free. I am now engaged in this investigation. At all events the organic substance is not cellulose, for no colour is produced below 212°, and there is an abundant evolution of carbonic acid.

A moderately-concentrated solution of caustic potash may also be employed to distinguish pyroxyline from the substance from which it has been prepared; it dissolves the pyroxyline with considerable ease, and without becoming much coloured. No cyanogen compound is found in this solution.

It appears that the differences which have been noticed by various observers, both with respect to the explosive force of pyroxyline in firearms, and likewise relative to the temperature at which this explosion takes place, must be attributed to the mode of drying, and especially to the greater or less rapidity with which the temperature is increased. In fact, I have seen some pyroxyline explode when heated quickly in a glass tube placed in an oil-bath, just as the thermometer indicated 270°; while by raising the temperature very slowly, I have succeeded in heating it each time much higher, as beyond 356°, and even 392°, without exploding. Surprised to find this body resist such elevated temperatures, I sought for the cause, and found that a temperature of 302°, continued for some time, sufficed to modify it entirely; it loses either nitrous or nitric acid, or deutoxide of nitrogen, which I have not yet been able to ascertain, and then burns like German tinder. Perhaps the pyroxyline has been converted into xyloidine. At 356° the substance becomes coloured yellow, and leaves a considerable carbonaceous residue on combustion.—*Comptes Rendus*, Dec. 21, 1846.

On a peculiar Acid resulting from the Action of Lime and Ferment on Crude Tartar. By J. Nicklès.

M. Noellner has described a peculiar acid, the pseudo-acetic, which had hitherto been confounded with acetic acid, and which he had observed in the acid fermentation of the dregs of wine in the presence of lime. The differences, according to that chemist, between acetic and the pseudo-acetic acid consist in the atomic weight of the latter, which is equal to 116 in the anhydrous state; in the salts of lead and soda, which crystallize in octahedra; and lastly, in

the property of the pseudo-acetates of gyrating upon water like the butyrates.

According to Berzelius, the pseudo-acetic acid is only a mixture of acetic and butyric acids.

M. Noellner having placed some of his acid at my disposal, I have undertaken its examination. Its composition, as well as its properties, confirm in every respect the opinion of the illustrious Swedish chemist. I have not succeeded in obtaining crystals of the lead or soda salt. These results leave undecided the question as to whether this acid is a mixture of acetic and butyric acids, or a peculiar acid which is modified by exposure to the air, like vaccinic acid for instance.

This kind of fermentation may often give rise to another product: I am indebted to the kindness of Prof. Liebig for a lead salt, the acid of which has the same origin as the preceding, but it possesses some very distinct properties. I regard it as containing the elements of acetic and butyric acids, and for that reason have called it *butyro-acetic acid*; its atomic weight, and the analyses of its salts of baryta, lime and silver, lead to the formula $C^6 H^5 O^4$. Its atomic weight was found to be 912; the calculated is 910.

The pure acid is obtained by liberating it from its combination with soda by means of phosphoric acid; the solution of the phosphate of soda becomes gradually covered with a stratum of oil, which is removed and rectified. Thus obtained, it is colourless, and of an odour slightly resembling that of butyric acid; it is soluble in water, alcohol and æther, and boils at about 288° F. Heated in a tube with potash and arsenious acid, it disengages the characteristic odour of alkarsine. All its salts produce at the surface of water a gyratory movement similar to that observed with the butyrates. In the crude state in which I received it, it was mixed with a little acetic acid, from which it is easily separated by means of baryta, with which it forms beautiful rhombic prisms. This salt is very soluble in water, but only to a slight extent in absolute alcohol. At 392° it loses 1 atom of water, and on analysis yielded the following results:—

Carbon.....	25·81	25·17	25·83	6 =	450·0	25·41
Hydrogen	..	3·57	3·58	5	62·5	3·52
Oxygen	..	17·12	16·45	3	300·0	16·97
Baryta.....	54·14	54·14	54·14	1	958·0	54·10

The mean of three determinations yielded the atomic weight 1773·18.

Heated to a dark red, this salt yielded an oily, odoriferous, inflammable body; but the quantity obtained was too small to decide whether it was the acetone of this acid or a mixture of butyrone and acetone.

The salt of lime, $C^6 H^5 O^3 CaO$, in the anhydrous state crystallizes in efflorescent needles; the silver salt, $C^6 H^5 O^3 AgO$, separates in dendritic crystals, which are altered by exposure to light. The copper salt crystallizes in oblique rhombic prisms; it is insoluble in water, but very soluble in alcohol. Heated suddenly, it is decom-

posed into carbonic acid and carburetted hydrogen; while a volatile liquid, composed of a mixture of butyro-acetic acid, and an oily substance, insoluble in water, distils over, and a residue of copper and carbon is left; but it does not yield any white deposit in the neck of the retort of a protosalt of copper similar to those obtained under the same circumstances from the acetate and butyrate.

On adding chloride of barium to a mixture of butyrate and acetate of lead, a precipitate of chloride of lead is obtained, a large amount of which redissolves; the same chloride is soluble in a mixture of butyrate and acetate of baryta without forming any stable combination. But if the butyro-acetic acid is really a peculiar acid containing the elements of acetic and butyric acids, not only this property of the barytic salt might occur, but it should moreover form a stable combination, as the latter would then no longer present the extraordinary case of three acids united to two oxides. And, in fact, the solution of chloride of lead in the butyro-acetate of baryta deposits, after some time, some small square prisms, which contain an equal number of equivalents of lead and barium; but not without having first deposited some crystalline crusts of chloride of lead.

I regret that the small quantity of material which I possessed did not admit of my examining the products of decomposition of this interesting acid. It is nevertheless certain that it possesses the same composition as metacetonic acid, but is not identical with it; the characters of its salts of silver, copper and baryta are directly opposed to such a view.

The properties of this acid lead us moreover to the opinion, that acetic and butyric acids, produced in the fermentation of the crude tartar under the influence of lime, may in certain cases, either during their formation or subsequently, group themselves so as to form a peculiar acid, differing by its properties from acetic and butyric acids considered separately, and also mixed, for its formula taken twice represents the sum of these two acids—

$$2(C^6\,H^5\,O^4) = C^4\,H^3\,O^4 + C^8\,H^7\,O^4.$$

It is not bibasic; its perfect volatility, boiling-point and mode of formation would not justify this opinion.—*Comptes Rendus*, xxiii. p. 419.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

An Account of an Attempt to prepare the Stannate of Soda on the Large Scale by a new Process. *By* Robert E. Brown, M.D., Edinburgh*.

There is a method, well-known and in common use among the calico-printers, of deoxidizing indigo, and of obtaining it dissolved

* Communicated by the Author.

in caustic soda, that it may be applied to cotton fabrics, by the process of boiling it in a solution of caustic soda along with metallic tin. It appeared to me that in this process the tin must become oxidized, and in all probability peroxidized, at the expense of the indigo, and that it must form stannate of soda :

$$2(C^{16}H^5N + O^2) + St = 2(C^{16}H^5N + O) + St\,O^2.$$

On examination I found that such was the case, and that by taking the solution of indigo, deoxidized in the manner above mentioned, and exposing it to the action of the air for some time, the indigo became reoxidized and insoluble ; and being separated by filtration, there remained a solution of stannate of soda, together with some excess of the alkali. The stannate of soda thus made was found on trial to answer exceedingly well for the preparation of cloth for what in the art of calico-printing are termed "steam colours;" and as the indigo might be repeatedly used in successive operations for an indefinite number of times, it undoubtedly might be made a practical process, and would be both more œconomical than the ordinary method of preparing it by neutralizing the oxymuriate of tin with caustic soda, and redissolving the precipitate in an excess of the alkali, and would give a purer substance and a more perfect solution to work with. I suggested the process to a gentleman connected with a calico-printing establishment in Lancashire, but I am not aware whether it has been carried into effect or not.

Indigo, however, would be a costly substance to work with in operations of any extent ; even with the most careful manipulation it would be impossible, in conducting the process on a large scale, to avoid the loss of some portion of it. On this account I sought for a material which might be substituted for the indigo, and which by its cheapness would not be liable to the same objection. It seemed to me that a metallic oxide, soluble in caustic soda, and the base of which was electro-negative to the tin, and at the same time insoluble in caustic soda, would fulfill the conditions I required. I therefore selected the protoxides of lead and of copper, as the only bodies which, by their cheapness and their ease of preparation, appeared likely to be of any practical use.

Accordingly I took a quantity of litharge, and boiling it in a solution of caustic soda along with some metallic tin, there immediately appeared a black precipitate, which on examination I found to be metallic lead. This went on increasing till the litharge disappeared, and all the lead was deposited in the state of a soft spongy mass. In my notes of some of the experiments I made upon the small scale, I find that I used the proportions and obtained the results undermentioned :—31·3 grs. or one equivalent of hydrated caustic soda were taken and dissolved in such a quantity of water as that the solution might stand about 30° of Twaddell's hydrometer, or spec. grav. 1·150. This was raised to the boiling temperature, and there were then added to it 111·5 grs., or about 1 equiv. of the ordinary litharge of commerce, and also a slip of metallic tin weighing 84 grs. Immediately the tin became coated with a bulky mass of

spongy metallic lead, which went on accumulating, till within the course of half an hour all the litharge had disappeared. The slip of tin was then weighed, and was found to have lost about 25·7 grs. in weight. By theory, supposing the litharge to have been a pure protoxide of lead, it ought to have lost 29·4 grs.; but the litharge of commerce always contains a certain portion of metallic lead, as evidenced by the evolution of nitrous acid fumes when it is dissolved in nitric acid; and this may account for the circumstance of less than one-half of an equivalent of tin having disappeared. When the liquid became cold, it was decanted from off the precipitated lead, and was found to be a transparent and colourless alkaline solution of stannate of soda. The lead was then very thoroughly washed and dried; and being touched with a red-hot iron, it took fire, and, burning like tinder, it became rechanged into litharge; which might be again employed in the same process, and which frequently was so.

The results of my experiments seemed to be so satisfactory, that I thought it worth while to attempt a process on a larger scale; and by the kindness of Mr. James Young, the manager of the chemical works of Messrs. Tennant, Clow and Co. at Manchester, I had every facility afforded me for doing so.

Accordingly, I took 9 lbs. of hydrated caustic soda, dissolved in as much water as was necessary to form a solution of the strength of 30° Twaddell, 13½ lbs. of granulated tin, and 56 lbs. of litharge. The relative proportions of these substances were nearly the following:—Caustic soda, 1½ equiv.; tin, 1 equiv.; litharge, 2 equivs. They were then boiled together for several hours. The action was very rapid; the metallic lead was precipitated in dense clouds and masses upon the tin, so that in the course of a few minutes it was impossible to recognise it by the eye, or in any other way than by touching it.

The results of this experiment showed the necessity of making certain alterations upon the manner of conducting the process. The granulated tin became so coated with the precipitated lead, that all further action upon it became impossible. Some portions of it were aggregated into masses, and these being tossed about by the ebullition of the liquid, formed hard and solid boulders; and the whole of the solid matters sinking to the bottom of the vessel in which the process was conducted, caked, and formed a layer impermeable to the heat of the fire. In consequence of these circumstances, a considerable part of the tin and of the litharge, not being acted upon, were lost to the process; and when the lead came to be burned back into litharge, it gave an imperfect and impure material. In addition to these defects, there was another, of a somewhat curious and unexpected nature, of which I may as well say a few words at present. A considerable portion of the tin, instead of being peroxidized and forming stannate of soda, remained dissolved in the liquid as the protoxide of tin. This puzzled me a good deal at the time, and I made a number of experiments to determine the cause of it, and to ascertain the conditions under which it took place. The result of these experiments showed that when there was an excess of tin em-

ployed, or when too large a surface of it was exposed, so much of it was dissolved that the litharge was insufficient for the perfect peroxidation of it all. I found that by the addition of more litharge to the liquid I obtained in the above-mentioned process, I could effect the peroxidation of the tin, and that in future operations I could avoid the recurrence of this effect, by stopping the operation as soon as the proper quantity of tin was dissolved.

To remedy these imperfections, I first made use of a solid bar of tin, and subsequently, in order to give an increase of surface, and so to hasten the process, I made use of several wedge-shaped slips of the metal. To prevent the precipitate from collecting at the bottom of the pot or boiler, I suspended a shallow square iron vessel in the centre of it, a few inches above the bottom. In this I put the litharge at the commencement of the process, and placed the tin plates so that it hung under them, and collected the lead as it detached itself from the tin plates, upon which for the most part it was precipitated. By means of these arrangements the process was very considerably improved and facilitated. The caking of the solid materials was prevented; the tin could be cleaned and kept in a fitter state for being acted upon; and being capable of removal when the proper quantity had been dissolved away, the formation of the protoxide was prevented.

But again new difficulties presented themselves; about the beginning of the process the action went on with extreme rapidity, so that in the course of half an hour's boiling I have seen the lead deposited upon the slips of tin in great spongy masses about half an inch or three-quarters of an inch in thickness. On shaking or scraping the tin, it fell off in handfulls, leaving the metal bright and clean, and permitting the action to be renewed with great vigour. But by-and-by the precipitate decreased in quantity; it lost its massive and spongy character, and became muddy; and at the same time there appeared upon the tin a thin black scale, which it was difficult to remove, and which was the source of disturbance to the operation.

I attempted to get rid of this obstacle in the following way:— I took a solid cylinder of tin, about a foot in length and 5 inches in diameter, mounted upon an iron axle, which rested and worked in "bushes," attached to two opposite sides of the square iron vessel I formerly mentioned as being placed within the pot, for the purpose of containing the litharge and collecting the precipitated lead. Upon one side of this vessel there was fixed a sharp iron scraper, which worked against the whole length of the cylinder of tin, and was pressed against it with considerable force by means of a weight attached to a lever. This scraper was about 3 inches in breadth, and had a back and sides attached to it. It resembled that part of the cylinder calico-printing machine which is technically termed the "doctor;" or more closely still it resembled that form of "colour box," belonging to the same machine, which is directly attached to the printing roller. The cylinder of tin was made to revolve against this scraper, and to turn off the lead precipitated upon it into the box at its back, by means of an endless chain working in a groove

at one end of the cylinder, and passing over a pulley, fixed above it, which was turned by a winch handle.

By means of this apparatus I succeeded in keeping the tin roller clear, and in getting rid of the lead as it was precipitated upon it. It was, however, ineffectual in removing the thin black scale which in the latter half of the process appeared upon the tin. On this account I abandoned it, and employed in preference large plates of tin, as being simpler, more easily managed, and as easily cleaned from the black scale.

What this black substance was I was unable to determine; for although it formed an opake and impermeable scale, yet the quantity of it was so trifling that it could not be collected for examination. It was suggested to me that it might be formed by the carbon and other impurities, which are always present to a small amount in tin, being left behind as the metal was dissolved away; but this explanation can hardly be correct, for when the tin plates, having been cleaned from this substance, were replaced in the liquid, it appeared again in a very short time, in a period very much less than it took to form at first; and this it ought not to have done had the above explanation been correct.

The other of the two circumstances which interrupted the process was the following:—After the boiling had gone on for 4 or 5 hours, the stannate of soda which had been formed in this time ceased in some measure to be soluble, and separated from the liquid in a solid form. This change took place suddenly, and was nearly coincident with the appearance of the black scale upon the tin of which I have already spoken. Up to the time of its appearance the liquid was perfectly transparent, or at least it became so when the portion of lead mechanically suspended in it by the ebullition of the boiling was allowed to settle down; but all at once the liquid became somewhat milky and opake, and by-and-by a copious white crystalline precipitate deposited itself. The crystals had a good deal of the appearance of fish scales, but they had no defined sides or edges. They varied in size from an eighth to a quarter of an inch in diameter. They were more soluble in cold than in hot water; and in consequence of this, the liquid, when it became cold, redissolved a good deal of that which was thrown down when it was boiling. When a quantity of it was put into cold water and allowed to stand for some time, a solution of it was formed of the strength of 50° Twaddell, or spec. grav. 1·250. From the examination I made of this precipitate, I came to the conclusion, that it chiefly consisted of stannate of soda in one of the many anomalous states in which the stannic acid and the stannates so frequently present themselves.

These two circumstances had the effect of deteriorating the process, by interrupting it at a stage when a sufficiency of stannic acid for the saturation of all the caustic soda had not been formed, nor nearly formed; consequently there remained a great excess of free caustic soda, which not only was quite lost and useless itself, but which, when the material came to be employed for the preparation of cloth by the calico-printer, would cause a still further loss to be

incurred, by the necessity it would occasion of using a much larger portion of acid for its neutralization, and for the precipitation of the stannic acid upon the cloth. In the experiments of which I speak, I took 16 lbs. of hydrated caustic soda, dissolved in water so as to form a liquid about the strength of 30° Twaddell, and 30 lbs. of litharge. These acted upon and dissolved 7 lbs. 4 oz. of metallic tin; and I found it to be so troublesome, that it amounted to an impracticability to get a greater quantity of tin dissolved. The equivalent relations of these quantities are nearly the following:—Tin, 1 equiv.; litharge, 2 equivs.; caustic soda, 4 equivs. These numbers show the great amount of caustic soda which is left unused and is lost. Apparently this difficulty might have been removed by collecting the precipitate of stannate of soda, which, as I have already mentioned, appeared in the course of the boiling, and by dissolving which in water, a solution, tolerably pure and free from caustic soda, might be obtained; but the circumstance of its not forming a solution above the density of 50° Twaddell interfered with this, as such a solution was much too bulky to be well adapted for commercial purposes. Stannate of soda in a dry and solid form might easily have been obtained by this process; but it was found that this would have interfered with the rights of Messrs. Howarth and Barnes, chemical manufacturers at Manchester, who had patented a process for the manufacture of this salt, by deflagrating tin along with nitrate of soda and caustic soda, and who had likewise secured the right of preparing stannate of soda in a dry form.

With regard to the precipitated lead, I have already incidentally mentioned, that I proposed, after washing it well, to heat and burn it back into oxide of lead, to be used again in subsequent processes. This operation I performed several times with perfect success. The lead was put upon the hearth of a furnace, such as is commonly used for burning metallic copper into its oxide; and when the lead had been previously very carefully washed and dried, the combustion took place with great readiness, resembling that of tinder or of slow touch-paper. I frequently employed the oxide of lead thus made, instead of litharge, in these experiments; and as it was in a more divided and less indurated state than the fused oxide of lead of commerce, the action was in the same degree more rapid and advantageous.

Had the process been available, the lead might have been turned to more useful account than as a mere piece of apparatus for oxidizing the tin. I observed that, after being thoroughly washed and allowed to stand exposed to the air for some time, it slowly became converted into the carbonate of lead. This operation was much hastened and facilitated by adding a little nitrate or acetate of lead to it, and keeping it wet and exposed to the air in a warm situation. There are several other ways in which it might have been made useful in the arts, but it is needless to mention more.

I am not aware that the foregoing observations have ever been noted or described before. It appears to me that they possess some degree

of intrinsic importance; and that they may be of interest, as suggestive of new experiments, applications and processes in chemistry, and more especially in organic chemistry, by the powerful and very manageable means they point out of oxidating and of deoxidating many substances to any definite or desired extent. The principle of the process may be applied in endlessly modified experiments. Other solvents may be used than caustic soda; other oxidating substances may be used besides indigo or litharge; and other deoxidating agents than tin. I shall have no opportunity of pursuing the matter further myself; but if these experiments should suggest any new objects of pursuit to others, they will not altogether have been made in vain.

Preparation of Oxide of Uranium. By T. H. Peters.

To avoid the use of a very large quantity of sulphuretted hydrogen, the pitchblende is dissolved in nitromuriatic acid, precipitated with ammonia, the precipitate digested with carbonate of ammonia, and the cobalt and copper separated by sulphuretted hydrogen from the ammoniacal solution. The solution of the oxide of uranium in carbonate of ammonia is now evaporated, when the oxide of uranium separates as a yellow powder, which is heated until the whole of the ammoniacal salt is removed.—*Archiv der Pharm.*, xlvii. p. 146.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Dec. 21, 1846. (The President, Professor Graham, in the Chair.)

"Extracts from a Letter to Dr. Hofmann by Baron Liebig."

Professor Liebig communicates the results of his most recent investigations in organic chemistry, which are highly interesting. He has succeeded in demonstrating, at last, the existence of both free lactic and phosphoric acids in the substance of the muscle of animals, although separated only by a thin membrane from the blood and other alkaline fluids in the vessels. To this difference in the condition of the solid muscle and fluids he attributes many of the galvanic effects observed by Matteucci. He has also confirmed the existence of the crystalline neutral substance creatine, first described by Chevreul, and discovered in flesh; and has also observed two new crystalline bodies, present in small quantities. While investigating the action of common salt in the animal œconomy, he finds that the fluids without the blood and lymphatic vessels contain only potash salts, namely chloride of potassium and phosphate of potash with phosphate of magnesia, while the blood and lymph contain only those of soda. The brine of salted meat abstracts the soluble phos-

phates, which are necessary to the formation of blood; and hence the scorbutic action of salted meat. The soup from boiled meat contains the soluble phosphates of the flesh, and the meat itself the insoluble. Neither the soup nor the boiled meat alone can therefore maintain the processes of life, but both must be taken together. It is also stated that, by the oxidation of caseine by the action of peroxide of manganese and sulphuric acid, M. Engelberger has obtained three curious products, namely aldehyde, essential oil of bitter almonds, and a fluid æthereal body with a composition analogous to metacetone; lastly, that proteine prepared by the new process of Mulder, and supposed by that chemist to be free from sulphur, still contains the element in question to the extent of $1\frac{1}{2}$ per cent.

"On the Salts of Sulphurous Acid," by James Sheridan Muspratt, Ph.D.

This is a second and extended examination of these salts in detail by the author, in which some points of difference in his own former results and those of M. Rammelsberg are explained.

"An Analysis of Bohemian Glass," by Mr. Rowney.

This is the glass so valuable for its infusibility in the construction of the combustion-tubes used in organic analysis. Although soda was found present to the extent of a quarter of the potash, the glass appears to be essentially a silicate of lime and potash, in which the oxygen in the silicic acid is to that in the bases as 6 to 1. It gave 73 per cent. silicic acid, $11\frac{1}{2}$ potash, 3 soda, $10\frac{1}{2}$ lime, with small quantities of alumina, peroxide of iron, magnesia and oxide of manganese, to make up the 100 parts.

Jan. 4, 1847. (James Lowe Wheeler, Esq., in the Chair.)

"Note on the Preparation of a Fixed Manure from Urine," by Dr. Robert Angus Smith.

This process consists in the addition of carbonate or sulphate of magnesia to the urine, by which the double phosphate of ammonia and magnesia is formed, in large and distinct crystals, easily separable from the liquid portion; and thus the most valuable parts of this manure may be brought into a form easy of transport, and may be made without much knowledge or trouble.

"On Thialdine and Selenaldine, two new artificial Organic Bases," by MM. Wöhler and Liebig.

On passing hydrosulphuric acid into an aqueous solution of aldehyde of ammonia containing a few drops of free ammonia, the authors produced a beautiful new base, free from oxygen, and containing a large amount of sulphur. This body, for which they propose the name of Thialdine, is obtained in large crystals, insoluble in water, but soluble in alcohol, and much more so in æther. It forms crystalline and well-defined salts with the acids.

The analyses of these bodies gave the following results:—

Thialdine.....	$C^{12}H^{13}NS^4$
The hydrochlorate.....	$C^{12}H^{13}NS^4$, HCl
The nitrate.....	$C^{12}H^{13}NS^4$, NO^5 HO

The following equation expresses the mode of formation of thialdine:—

$$\underbrace{3(NH^4\,O, C^4\,H^3\,O)}_{\text{Aldehydite of ammonia.}} + 6HS = \underbrace{C^{12}\,H^{13}\,NS^4}_{\text{Thialdine.}} + 6HO + \underbrace{2NH^4\,S.}_{\text{Sulphide of ammonia.}}$$

On substituting hydroselenic acid for hydrosulphuric, the corresponding selenium compound, the selenaldine, is obtained, which, though resembling very much the former base, is far more liable to decomposition.

"Some Remarks on the Air and Water of Towns," by Dr. R. A. Smith.

Having given some attention to the inquiry into the health of towns, the author was anxious to find what the real evil in the polluted atmosphere of towns consisted of; and in furtherance of this object commenced a series of examinations on the water used in the town of Manchester for ordinary purposes. Rain-water, collected in cisterns, was first examined; and on heating the solid matter obtained by evaporation, it burnt, giving the odour of fat, and a strong smell of nitrogenized organic matter. Rain collected in a clean porcelain dish, and treated in the same way, gave indications of a similar kind, but in a smaller degree. The moisture condensed from the breath contained organic matter in large quantities; and when collected from the windows of crowded rooms, it smelt strongly of human sweat during the evaporation; and when the solid residue was heated, it gave the odour of burning flesh. Water from a great number of wells situated in Manchester was submitted to examination, and in all similar results were obtained. Dr. Smith finds also that the water of rivers and canals becomes contaminated in this way as soon as it reaches a town. The proportion of nitrates is also in many cases remarkable, arising from the rapid oxidation of these nitrogenized ingredients. The author concludes by stating that he is pursuing this investigation at various seasons, so as to make a more complete examination of the subject; and the whole of the analytical results will then be given.

THE CHEMICAL GAZETTE.

No. CIV.—February 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Elementary Composition of the Potato whilst forming a succession of Tubers, as observed during the year 1846. *By* Geo. Kemp, M.D. Cantab. F.C.P.S.

The following research is in continuation of a similar investigation conducted during the autumn and winter of 1845; the specific object being to elicit, by means of ultimate analysis, whether any or what changes the potato tuber undergoes whilst suffering from what has been denominated the potato blight. It seemed sufficiently apparent, that any hypothesis with reference to its cause, or suggestions of a remedial character, would at least be premature before the nature of the affection was determined. The whole of the subsequent history fully confirms the opinion; for as yet we are confessedly as far off as ever from any directions for the future guidance of the agriculturist. The reasoning on the subject seems to be assuming a circular character; and incidental occurrences, such as the existence of fungi and insects, are still confidently put forward as the causes of this fell calamity.

Leaving the naturalist to determine how far the presence of the above circumstances have a just claim to the important position assigned them, the author begs, with as much brevity and conciseness as possible, to state the results of the application of one department of practical science; with the full conviction that they have a tendency to place future inquiry in a more hopeful condition, and to connect observations which have hitherto retained a mere isolated position.

It will be necessary, in the first place, to revert to the labours of the preceding year, which formed the materials for a paper read before the Cambridge Philosophical Society. That a subject involved in so much obscurity would present difficulties of a formidable nature will be readily admitted; and not the least of these was the determination of a fixed point, on which all the facts of the case should directly bear, and towards which all the deductions, of whatever nature, should converge. On consideration it seemed apparent, that if the composition of a tuber perfectly free from disease were selected as the type, and with this the composition of the tuber when completely degenerated were compared, the character of the

disintegration would be determined; but something more than this was necessary. The merely establishing the existence of a specific change in the relative proportions of the organic elements would remain practically useless, unless connected with the known operations which are ever influencing organized matter, either by inducing it, under the agency of vitality, to assume new forms for the performance of new functions, or, that agency ceasing, again to assume those inorganic compounds from which, as an organized whole, it originally sprang. At the onset of the inquiry the mind was instinctively led to the latter of these as most likely to have occurred; in fact, that the changes effected were analogous to those produced by what is denominated putrefactive fermentation; this opinion, however, was negatived by subsequent research.

The analysis of the sound tuber by Bonssingault was selected as the ground-work of comparison, both from the high reputation of the analyst, and the object for which its examination was instituted being totally unconnected with the present inquiry, at a period indeed long antecedent to it. The following was its composition:—

Carbon	44·1
Hydrogen	5·8
Nitrogen	1·2
Oxygen	43·9
Ash	5·0
	100·0

A potato tuber which was undergoing the morbid changes, a portion however remaining apparently sound, gave the following results:—

	Sound portion.		Unsound portion.		
	I.	II.	I.	II.	III.
Organic matter	95·75	95·86	94·22	94·45	94·29
Inorganic matter	4·25	4·14	5·78	5·55	5·71
	100·00	100·00	100·00	100·00	100·00

The unsound portion, submitted to ultimate analysis, gave—

	I.	II.	III.
Carbon	42·09	41·73	41·99
Hydrogen	7·02	6·56	7·02
Nitrogen	1·23	1·23	1·23
Oxygen	43·98	44·80	44·08
Ash	5·68	5·68	5·68
	100·00	100·00	100·00

Having thus determined that a total change of composition had been effected, it became necessary to adopt some method for eliciting the nature of the change itself and the agencies by which it had been accomplished. The writer would have scrupled to obtrude his theoretical views on the public, had not the result proved the correctness of his deductions in a manner not easily controverted; and

he trusts that the method of approximations which were successful in this case are destined to elicit many important facts which are as yet involved in obscurity.

It must be conceded that chemical formulæ have recently been employed in such a manner as considerably to lessen their value in the eyes of those who attach more importance to facts well made out than to brilliant speculations. Inexperience, on one hand, and deeply-rooted preconceived opinions, on the other, have, in many cases, substituted the lowest degree of moral evidence for demonstration; and methods of approximation, of great value where no better means are at hand for solving physiological problems, have been employed, to the exclusion and prejudice of analytical investigation. An indistinct apprehension of the respective value and adaptation of the different kinds of formulæ has also been the evident cause of much error and misconception. The writer has been accustomed, for his own guidance, to arrange the general expressions alluded to under five classes:—

1. Those which are deduced from the quantity of the unknown body, as compared with the quantity of any known body with which it has a tendency to combine. In this case it is clear that the known body must be considered constant, and distinctly treated as such. This remark would be superfluous did we not observe instances in which the quantity of the known body in the formula does not correspond with that found. Such formulæ must excite suspicion, for if the quantity be so altered as to modify the general expression, they are faultily deduced; if the alteration be too trivial to produce such a result, it can only have been made for the purpose of trimming up the figures of the other elements.

2. Indirect rational formulæ, expressive of bodies which, although incapable of entering into definite combination with known bodies, stand in so well-determined a relation to such, that no doubt can exist as to their constitution. Numerous instances occur between the limits $C^{12} H^8 O^8$ and $C^{12} H^{14} O^{14}$.

3. Empirical formulæ, which, whilst they accurately express the facts of the analysis, are so arranged as to show the relation of the body in question to others from which it may be derived or into which it may be resolved; in fact, to develope its alliances, and from these to deduce its probable constitution. The degree of probability will of course be dependent on the nature of the body to which it is assumed to be related, and the accuracy with which the different causes which have operated to occasion its difference can be traced. Such are the formulæ principally employed in the physiological department of chemistry; they are merely expressive of probabilities, not of facts, any further indeed than they accord with the analysis; they cannot, in any case, be legitimately used in the place of rational formulæ, and must be rigidly subjected to all the laws of moral evidence generally.

4. A class of expressions still lower in the scale of evidence and more limited in application. The quantities of the different elements can be determined, but the body expressed can only be referred to

its original by approximation, involving known sources of error. These formulæ can only be used as indicative of processes; not, like many of the former, as determining quantities; with proper precaution, however, they are of considerable practical value where other modes of investigation are not at our disposal; and it is by their application that the nature of the changes occurring in the potato disease has been traced.

5. Cases occasionally occur, in which, from the smallness of the quantity at our disposal, only two of the organic elements can be determined; even these however can often, with care, be arranged in a useful form, but have nothing to do with the present inquiry.

Returning from this digression to the analysis of the sound potato by Boussingault, it is assumed that the tuber of the potato, as well as the seed, may, so far as its ultimate composition is concerned, be considered as made up of two portions, the one containing nitrogen, the other destitute of that element. It is a fact, well determined by Einhof, Lampadius and Henry, that the non-nitrogenized portion is either starch or bodies comprised under the same organic group; and that the smaller nitrogenized portion is albumen or a body analogous to it. We proceed then to construct a formula, which shall at once express the results of the actual analysis, and at the same time include the above proximate elements. Considering, in fact, that the whole of the nitrogen, not being in the form of salts of ammonia, is due to the organic group represented by anhydrous proteine as a type, and taking 5 equivs. of nitrogen as our constant, we obtain the formula $C^{436}H^{343}N^{5}O^{324}$, giving in 100 parts—

	Calculated.	Found.
Carbon	44·2	44·1
Hydrogen	5·7	5·8
Nitrogen	1·2	1·2
Oxygen	43·9	43·9
Ash	5·0	5·0
	100·0	100·0

If from this we subtract Mulder's formula for anhydrous proteine, $C^{40}H^{31}N^{5}O^{12}$, we obtain as a residue the formula $C^{396}H^{312}O^{312}$; which is at once recognised as arranging itself in the same group with starch, and can, in fact, by the addition of 18 equivs. of water, be considered as representing 33 equivs. of that body. Proximate analyses prove that, in the tuber, this aggregate is composed of a large proportion of starch, with cellulose, gum, and analogous substances.

Let us now observe precisely the same conditions with reference to the tuber undergoing the disease in its most exaggerated form. The formula deduced is $C^{400}H^{407}N^{5}O^{316}$, giving a per-centage—

Carbon	41·87
Hydrogen	7·09
Nitrogen	1·23
Oxygen	44·12
Ash	5·69
	100·00

Deducting, as before, the formula for anhydrous proteine, we obtain the remainder, $C^{360}H^{376}O^{304}$. Here it is evident that the non-nitrogenized portion has undergone a total change; and the question for solution is, Are we acquainted with any organic processes to which such a change may be reasonably attributed? The researches of Erdmann and Marchand in 1843, as well as of Scharling in 1844, proved that during the germination of seeds and tubers, that of the potato being specified, a change, perfectly analogous to the above, if not identical with it, occurred; that, in fact, butyric acid was formed, or, in other words, that the body represented originally by $C^{12}H^{10}O^{10}$ assumed a form in which the proportions of hydrogen and oxygen were no longer numerically the same, but $C^{8}H^{6}O^{2}$, or, which is the same thing as an empirical formula, $C^{12}H^{9}O^{3}$, that the usual deoxidizing agency of germination had effected the change; and by comparing this discovery with the above, we see the analogy; for 18 equivs. of starch, 18 equivs. of butyric acid and 88 equivs. of water give the formula $C^{360}H^{376}O^{304}$. The writer therefore did not hesitate to hazard the conclusion, that the nature of the disease in the potato tuber is an abnormal tendency to premature germination.

Such is a condensed view of the research during the year 1845; and, before proceeding to the details of the subsequent investigation, the reader is requested to bear in mind that the above formulæ are used strictly as indicating processes; they cannot be legitimately employed as determining quantities, or even specific proximate forms. The writer does not himself believe that the whole of the 18 equivs. of butyric acid existed in that condition, but rather, in a great part, as $C^{12}H^{9}O^{3}$; which, from an examination of the processes which take place in digestion, he has been led to consider as the first form of the disintegration of amylogenic bodies; nor can the water be considered as existing in that state, but as the elements of water, forming an integral portion of an organic group.

It was our national misfortune again to be visited with the potato blight during the year 1846; and, months after the conclusion of the above research, but very early in the appearance of the crop, our attention was called to a singular and, by all accounts, uncommon tendency of the tuber, shortly after its bulbing, again to germinate; the fresh sprout formed another tuber; and this again, proceeding in a similar manner, exhibited eventually a series of successive generations of tubers. Nature was now clearly and intelligibly pointing out the path for research. This tuberation, in many cases, went on to some extent without the appearances indicative of disease; in others, the disease and unnatural form of germination were consentaneous; here then were the means of connecting the extreme points of the research. In the previous year the sound tuber was compared with one in which morbid action had developed itself to its maximum; now we had an opportunity of tracing the phænomenon through its earliest development and progressive course.

Two specimens were selected for examination; the one, a series

of tubers free from disease; the other, a series in which the morbid process had commenced.

Examination of the First Series.

As the ground from which these potatoes were taken up was dry, the soil was removed without difficulty; and, to ensure the removal of the whole, the epidermis was rubbed off likewise, which was easily effected, as the tubers were in an early stage of growth. Having cut the whole into thin slices, they were placed under the receiver of the air-pump, and dried over sulphuric acid; the mass was then reduced to a powder, heated in an oil-bath at 110° C., again placed under the receiver, and thus prepared for analysis.

The ash amounted only to 3·66 per cent.

The ultimate analysis gave the following results:—

	I.	II.
Carbon	41·53	41·27
Hydrogen	6·82	6·85
Nitrogen	1·25	1·25
Oxygen	46·74	46·97
Ash	3·66	3·66
	100·00	100·00

Proceeding as above, these quantities may be expressed by the formula $C^{400}H^{879}N^{5}O^{336}$, which gives—

Carbon	41·6
Hydrogen	6·6
Nitrogen	1·2
Oxygen	46·9
Ash	3·7
	100·0

By deducting Mulder's formula for anhydrous proteine, we have $C^{360}H^{348}O^{324}$, as representing the amylogenic portion; and it will at once be observed that the balance of elements has been destroyed; in fact, that a mode of re-arrangement has commenced, perfectly analogous to what has been developed by the analysis of the tuber in the last stage of disintegration; for

$$C^{360}H^{348}O^{324} = (C^{312}H^{312}O^{312}) + (C^{48}H^{36}O^{12}),$$

the former of which evidently belongs to the group of bodies lying between the limits $C^{12}H^{8}O^{8}$ and $C^{12}H^{14}O^{14}$, and the latter is a multiple of $C^{12}H^{9}O^{9}$. Can it reasonably be doubted that the mode adopted for connecting the points of this difficult inquiry is legitimate?

Examination of the Second Series.

The potato in this case was undergoing the morbid changes usually observed, that is to say, the leaves were withered and infected with insects and mould; the tuber also had, extensively, patches of fungi under the epidermis. Elementary analysis gave the following result:—

	I.	II.
Carbon	45·17	45·19
Hydrogen	7·90	8·19
Nitrogen	1·30	1·30
Oxygen	41·11	40·80
Ash	4·52	4·52
	100·00	100·00

The relative proportions of the hydrogen and oxygen, in this case, at once indicate that the same changes have taken place, but to a greater extent. Unlike the former series, the temperature at which it was dried had partially decomposed the substance, and the same reliance cannot therefore be placed upon it. Confessedly imperfect however as the research is, the following conclusions will probably be admitted:—

1. That the morbid affection consists of a premature tendency to assume the organic changes which are consentaneous with, and essential to, the process of germination.

2. That the presence of fungi and insects do not account for these changes, and cannot therefore be considered as their exciting cause.

3. That the cause must be sought for amongst those agents which induce the process of germination in seeds and tubers; and

4. That a wide field is opened for analytical investigation, in order to elicit the mode of action and relative importance of such agents, as well as the peculiar conditions under which their agency becomes developed. It cannot be doubted that well-conducted research is capable of removing much of the obscurity in which this subject is involved, and, in all probability, of discovering principles important in their relations to the chemistry of germination generally.

St. John's, Isle of Man, Feb. 2, 1847.

On Lactucone. By G. A. Lenoir.

Lactucarium, the inspissated juice of *Lactuca virosa*, has frequently been the object of investigation; but no satisfactory information respecting its constituents have been hitherto published. Having in my possession some remarkably fine genuine lactucarium, I have repeated most of these experiments in the laboratory at Göttingen; and although they afford no information respecting the active constituent, which is probably an organic base, yet I think they show that what Walz and Aubergier have regarded as such is a peculiar indifferent body, hitherto unknown in the pure state, and the properties and composition of which I shall proceed to describe. The lactucarium which I employed was procured from the district of the Moselle, where it is obtained in a very simple manner, by making incisions with a silver knife in the plants of *Lactuca virosa*, which occur there abundantly in a wild state, and collecting the juice in cups, in which it is dried. The mass is then cut into square pieces about half an inch in size, and sent into the market. On

the surface it is more or less yellowish-brown according to age; upon a fresh fracture it is white, and possesses a remarkable opium-like odour.

The lactucone is obtained in the following manner:—Lactucarium, cut into fine pieces, is repeatedly extracted with boiling alcohol, and the solutions filtered boiling hot; on cooling, the greater portion of the lactucone separates in warty aggregations. It is still contaminated by a colouring and bitter substance, but is readily obtained pure by frequent recrystallization from alcohol and treatment with good animal charcoal. Lactucone crystallizes in minute colourless prisms, united in radiate or warty masses; when not quite pure, it is deposited, even though perfectly colourless, in amorphous verrucoid masses. It crystallizes best from naphtha, is perfectly void of taste and smell, and appears to have no action on the organism, as I did not feel the least effect after taking considerable quantities. It is almost insoluble in water, but readily soluble in alcohol, æther, essential and fatty oils. It melts, without experiencing decomposition, between 302° and 392° F.; I found it impossible to determine this more accurately, as it becomes amorphous. On solidification it forms a transparent amorphous mass. It is not volatile, but creeps up the sides of the vessel; a portion is destroyed, and yields a remarkable quantity of acetic acid. In a current of carbonic acid, on the contrary, it may be volatilized for the greater part undecomposed; in this operation a similar odour is perceived as when caoutchouc is melted.

Lactucone is a highly indifferent substance. I have not succeeded in combining it with any other body. Concentrated caustic potash dissolved in water or in alcohol has no action upon it; the same is the case with chlorine. Its solution in alcohol is not precipitated by alcoholic solutions of the metallic salts. Heated with soda-lime, it does not give off a trace of ammonia, and consequently contains no nitrogen; it was burnt with oxide of copper, with the application of oxygen gas towards the conclusion, and yielded—

Carbon.....	81·18	80·56	81·25	40	= 81·12
Hydrogen.....	10·91	11·33	11·09	32	10·78
Oxygen.....	7·91	8·11	7·66	3	8·10

which corresponds nearest to the formula $C^{40}H^{32}O^3$; it would consequently differ from betuline only by containing 1 equiv. hydrogen less; and it is indeed so nearly related in its properties, that I was at first inclined to regard it as betuline; however, it differs essentially from this in several points. Betuline is far more volatile, diffuses a different odour, and after melting always solidifies to a very crystalline mass, while lactucone constantly remains amorphous even after the most careful melting.—Liebig's *Annalen*, October 1846.

On the Decomposition of the Nitrite of Ammonia. *By* E. Millon.

An aqueous solution of nitrite of ammonia is decomposed by heat into nitrogen and water, according to the following equation:—

$$NO^3, NH^3, HO = 2N + 4HO.$$

On examining this reaction, I found that sometimes it was produced very rapidly, almost spontaneously, while at other times it proceeded with the greatest difficulty. A solution of nitrite of ammonia, contained in a thin glass tube, may be preserved for hours in boiling water without the least sign of decomposition; it is merely requisite to add to the dissolved nitrite 1 drop of caustic ammonia; while the same solution, immersed in the same water-bath, may be instantly destroyed, accompanied by a violent effervescence, when, instead of an alkali, a drop of either nitric, hydrochloric or sulphuric acid is added. This experiment led me to a very easy method of preparing the nitrite of ammonia. I pass very gradually into an excess of caustic ammonia the nitrous product resulting from the distillation of nitrate of lead; the ammonia is placed in a platinum crucible, and surrounded by a cooling mixture. The solution is evaporated over lime in a confined atmosphere saturated with ammoniacal gas. —*Ann. de Chim. et de Phys.*, February 1847.

Observations on Madder. By Dr. J. Shiel.

The opinion has been broached, that the various pigments contained in the root of the madder are probably oxides of one and the same radical; no actual investigation, however, in support of this view exists; the only analyses with which we are acquainted of any of the madder colours is that of alizarine by Robiquet, who assigns to it the formula $C^{37}H^{24}O^{10}$. This analysis, however, has been rendered perfectly valueless by the investigations of Runge, who showed that several volatile pigments are contained in the madder. The highly valuable microscopic examination of Decaisne showed that the red pigments are not perceptible in the fresh root.

The greatest difficulty which is met with in examining the madder pigments is the separating of them from one another. After numerous experiments, I found the following process the most advantageous*. The ground madder root was treated with water in a wooden vat, and left undisturbed for one or two days, the water poured off, and the madder, after being pressed, repeatedly extracted with a boiling concentrated solution of alum in a copper boiler. The filtered decoction deposits on cooling a reddish-brown substance, which may be separated by filtration. When the clear red liquid thus obtained is mixed with sulphuric acid, the dissolved pigment generally separates in the course of 24 hours, and the liquid is then but very faintly coloured; the pigment is collected on a filter, and dissolved in a boiling solution of alum. If a fresh deposit is formed on cooling, it is separated by filtration, and the liquid again treated with sulphuric acid. The precipitate thus obtained is washed with dilute boiling muriatic acid, and afterwards with cold water, and dissolved in alcohol, the greater portion of the alcohol distilled off, and then left to spontaneous evaporation. The madder-purple which is

* The experiments were all made with Baden madder, which is the same kind as the Alsatian.

deposited is dissolved repeatedly in æther, about two-thirds of the æther each time removed by distillation, and the remainder allowed to evaporate, when the pigment gradually separates.

The madder-purple obtained in this manner forms a brilliant cherry-red powder, which is scarcely soluble in cold water, tolerably so in boiling, and very readily soluble in alcohol and æther. It dissolves in alkalies of a dark red colour, from which it is precipitated by acids in red flakes. When heated, it melts, and is volatilized, apparently however undergoing some change. If the sealed end of a glass tube, about $2\frac{1}{2}$ inches long and some lines in diameter, is blown out into a bulb, a small quantity of the purple conveyed into the bulb, and this immersed together with a thermometer in a platinum crucible, of moderate size, half-filled with oil, and heat applied, the portion of the tube projecting out of the oil becomes coated at 437° with a violet film; and if the temperature is raised, this portion of the tube is gradually filled with minute crystals of the pigment. This property of madder-purple is opposed to the statement of Runge, according to whom the sublimed madder-purple is not crystalline. On filling a small platinum crucible of about 3 centimetres in height one-fourth full with madder-purple, placing a small funnel stopped with some paper over the crucible, and cautiously heating over the lamp in a sand-bath, I obtained a quantity of the most beautiful crystals of a cherry-red colour, some of which were $2\frac{1}{2}$ centimetres in length. These crystals however no longer yielded with potash a red, but a violet solution; the residuary portion in the crucible affords, when it has not been heated too strongly, the same violet colour with potash. Madder-purple yielded on analysis—

Carbon	56·71	56·64	28 =	56·71
Hydrogen	3·53	3·43	10	3·35
Oxygen	39·76	39·93	15	39·94

I may observe that all the pigments that were submitted to analysis were dried between 239° and 248°, and exhibited no trace of impurity under the microscope.

The behaviour of the madder pigments towards concentrated sulphuric acid is of vast importance in the manufacture of garancine. When madder-purple or madder-red, or a mixture of the two, is dissolved in cold concentrated sulphuric acid, the solution is of a splendid cherry-red colour; if to this solution from one-fourth to one-third of its volume of water be added, the colouring matter separates unaltered from the hot liquid. If the solution of the pigments in concentrated sulphuric acid is heated to 230°, the pigments are not altered even at this temperature; they separate unchanged when the still hot solution is cautiously poured into a vessel containing water. If, in the preparation of garancine, the sulphuric acid is diluted with one-fourth to one-third of its volume of water, there is no reason to fear any considerable quantity of the pigment being dissolved in it; nevertheless an acid of this strength immediately blackens a shaving immersed in it. The employment of too concentrated an acid has,

judging from this behaviour, the disadvantage that the flakes of pigment which separate on dilution are readily carried away by the wash-water. From the above experiments, moreover, it is evident that there is no need for so much anxiety respecting the temperature in the preparation of garancine, as many directions given in chemical works would make it appear.

Sublimed Madder-purple.—I have already mentioned that I obtained this body in beautiful crystals; indeed this substance is one of the most beautiful that is met with in chemistry. I was never able to effect the sublimation without producing a considerable carbonaceous residue. Its behaviour towards alkalies shows that the madder-purple experiences some change during the sublimation, which is also confirmed by analysis; for it yielded—

Carbon	53·30
Hydrogen	5·19
Oxygen	40·51

The expression $C^7 H^4 O^4$ includes 53·84 per cent. carbon and 5·12 hydrogen. I possessed too little material to make further inquiry into the kind of change; but in one experiment with a small quantity, I obtained, when the temperature was raised very cautiously, a considerable quantity of carbonic acid.

According to the statement of Robiquet and Colin, the crystals of alizarine are accompanied by a fatty substance, which prevents their dissolving in water; this substance is said to be removed by moistening with alcohol, and the alizarine rendered soluble. The assumption of a fatty substance is undoubtedly founded upon some error. If sublimed or unsublimed madder-purple or madder-red is moistened with a few drops of alcohol, the pigment, which alone is not soluble in water, passes with the alcohol on mixing with water into solution; the same happens when they are just moistened with æther, in order to remove the supposed fatty substance. The crystals of the sublimed madder-purple dissolve with difficulty in a boiling solution of alum; their solubility is increased by reducing them to powder.

Madder-red.—This substance is contained in the precipitate which subsides from the hot decoction on cooling; if this deposit be boiled with alcohol to which a concentrated solution of alum has been added, there is obtained on cooling two strata of pigments; the upper bright red flocculent layer is removed with a pipette, and some of the above mixture of alcohol and solution of alum poured upon the lower dark brown deposit, which is then heated, and again treated as above. I have repeated this treatment more than fifteen times, and have always obtained the upper bright red layer in whatever proportion the mixture of alcohol and water was employed; the quantity of the brown substance had diminished nearly two-thirds during this operation. When the flakes of the upper layer produce a pure violet solution with potash, the brown sediment is washed after their removal with dilute boiling muriatic acid, and afterwards with water, dried, and treated with boiling alcohol, which

dissolves the madder-red, leaving behind a brown substance. The alcohol is distilled off, the pigment dissolved in æther, a portion of the æther removed by distillation, the solution then left to spontaneous evaporation; and, when the greater portion of the pigment has separated, the remainder poured off. The treatment with æther is repeated until a powder of a pure brilliant yellow colour is obtained.

Madder-red is very sparingly soluble in water, but readily so in alcohol and in æther; with potash it yields a violet solution; ammonia and the fixed alkaline carbonates dissolve it with a red colour. It behaves, when heated, quite analogous to madder-purple; at 437° it begins to volatilize, and is deposited in beautiful orange-yellow needles. I have endeavoured to reduce both madder-red and madder-purple according to Preusser's method, but without success. A small quantity of madder-red, submitted to analysis, yielded the following results:—

		Equivalents.	
Carbon	67·20	28 =	67·43
Hydrogen	3·93	9	3·61
Oxygen	28·87	9	28·96

The formula $C^{28} H^{9} O^{9}$, as well as the preceding ones, must only be regarded as convenient expressions of the analytical results.

Sublimed Madder-red.—The behaviour of this substance agrees with that of the unsublimed pigment; the crystals are not soluble in water, but dissolve with ease in æther and alcohol. It is probable that its composition does not differ, although the analysis yielded a somewhat different result, viz.—

Carbon	67·71
Hydrogen	4·51
Oxygen	27·78

It appears to result, from the preceding observations, that madder-red may pass into madder-purple by the assimilation of 1 equiv. water and 5 equivs. oxygen,

$$C^{28} H^{9} O^{9} + HO + 5O = C^{28} H^{10} O^{15}.$$

If we adopt the formula $C^{28} H^{16} O^{16}$ instead of $C^{7} H^{4} O^{4}$, the sublimed purple differs from the red pigment only in containing 7 more equivs. of water.

The author then details some experiments which he made with a view of ascertaining the action of oxygen upon these pigments; madder-purple did not absorb half a cubic centimetre of the gas during 48 hours' confinement in a tube filled with oxygen, and remained unaltered; madder-red appeared to become converted into the purple pigment, for in attempting to close with the blowpipe the apparatus containing the madder-red, an explosion resulted, and the substance was scattered in all directions; at several parts of the tube there were dark circular spots; and what was collected of the substance was of a brown colour, and no longer yielded with potash a violet, but a red solution.—Liebig's *Annalen*, October 1846.

Researches in Animal Chemistry. By J. Liebig*.

It has long been known that the flesh of animals recently killed exhibits a perceptibly acid reaction. This property has been attributed by Berzelius to the existence of lactic acid, without however this fact having hitherto been confirmed by satisfactory analytical results. Several chemists have admitted the presence of lactic acid in the urine, gastric juice, and in the milk; but they supported their conclusion merely upon reactions, which are not trustworthy. Even the opinion that lactic acid prevents the precipitation of oxide of copper by milk of lime is founded upon an error. M. Strecker has recently shown that pure lactate of copper is entirely decomposed by milk of lime, and not a trace of oxide of copper can be detected in the liquid. It is true that the pure lactate of lime dissolves a trace of oxide of copper, but a slight excess of lime-water precipitates it completely. My researches were made with a view to do away with all uncertainty with respect to the non-volatile organic acid, which constitutes a part of the animal organism.

When the flesh of animals recently killed and chopped into a fine pulp is washed with cold water, a reddish liquid is obtained, which when boiled yields a coagulum of albumen and is almost entirely decolorized. The clear scarcely-yellowish liquid obtained in this manner is decidedly acid, and has a very aromatic and agreeable taste of broth. When neutralized with barytic water, phosphate of baryta and phosphate of magnesia are precipitated; it becomes slightly alkaline, without any baryta remaining in the solution. After the separation of these precipitates, crystals of creatine, discovered by M. Chevreul in meat broth, may be obtained by suitable evaporation.

On carrying the concentration further, acicular crystals are seen to form in the syrupy liquid, which, separated by filtration and purified by recrystallization, form white needles of a very brilliant nacreous lustre, and are very sparingly soluble in alcohol. The liquid separated from these crystals congeals to a thick mass, consisting of a syrupy mother-water and some very slender crystals in concentric groups, which are very soluble in alcohol, and even in a mixture of alcohol and æther. These two crystalline substances are potash or lime salts of two new acids containing nitrogen.

The last mother-water contains lactate of potash. To extract the free lactic acid, I treat this mother-water with alcohol, and add to it some oxalic acid likewise dissolved in alcohol, by which means I separate the potash as oxalate of potash. I then add æther as long as the liquid becomes turbid, by which I separate several other substances, and the alcoholic solution retains the lactic acid capable of yielding with hydrated lime lactate of lime, which admits of obtaining the free lactic acid and other lactates. On submitting to analysis the lactate of lime and that of zinc prepared in this manner, I obtained for the first the formula $C^6 H^5 O^5 + CaO + 4aq$, and for the

* A short notice of these researches appeared in our last Number.

second $C^6 H^5 O^2 ZnO + 2aq$. These results leave no doubt as to the nature of the non-volatile organic acid diffused through the animal organism; they explain the quick reaction of the muscles; and now that we know that there exists in so large a portion of the body of animals an acid liquid, which is only separated from an alkaline fluid (the blood and the lymph) by very thin membranes, we may, I think, explain several electrical phænomena observed by Matteucci and other physiologists upon the bodies of dead animals.

By employing several hundred pounds of flesh, I obtained a sufficient quantity of creatine to be able to submit this body to a careful examination. Its physical properties have been described by M. Chevreul with such precision that I have nothing to add on this subject. From my experiments I am led to conclude that creatine forms part of the flesh in all classes of animals; hitherto I have ascertained its presence in beef, veal, mutton, pork, horse-flesh, hare, fowl and pike. The beautiful discovery of that illustrious chemist becomes the more important, as there is no doubt that creatine acts an important part in the vital phænomena. It is at least certain that the flesh-broth cannot be replaced by gelatine, nor by any liquid obtained from any other part of the animal organism except the muscles. I have found creatine in bullock's heart, but not in the brain, liver, lungs or kidneys. Creatine belongs, from its crystalline form, to the clinorhomboidal system; it frequently yields tolerably large limpid crystals, which are transparent and possess great lustre; at 212° they lose 12·18 per cent. of water, which corresponds to 2 atoms. From numerous analyses I have obtained for the composition of crystallized creatine the formula $C^8 N^3 H^{11} O^6$.

Creatine is a neutral body, which dissolves in weak alkaline or acid liquids without experiencing any alteration; but its properties are changed in the presence of concentrated acids or of the caustic alkalies. Strong acids convert it into an organic base, which possesses some very remarkable properties; I have called it *creatinine*. It is formed in the presence of hydrochloric and sulphuric acids by the mere elimination of 4 atoms of water. On analysis it yielded the formula $C^8 N^3 H^7 O^2$.

Creatinine is far more soluble in water and alcohol than creatine; its aqueous solution is caustic to the taste, like ammonia; it turns red litmus-paper blue, and combines with all the acids, forming salts of great beauty; its platinum salt is remarkable, from the size of the crystals and its beautiful golden colour. The formula above given expresses the quantity which combines with 1 equiv. of acid. The crystals of creatinine belong to the monoclinometric system; they are bulky, colourless, and possess great lustre.

Creatine contains the elements of glycocolle (anhydrous sugar of gelatine) + 1 atom of ammonia; creatinine, those of cafeine + 1 atom of amide. I may add that 40 thin fowls yielded about 24 grms. of creatine; 56 lbs. of beef, 16 grms.; and 100 lbs. of horse-flesh, 36 grms.

The extracts of the different kinds of flesh upon which I experimented leave, on evaporation to dryness and calcination, a white ash,

which contains phosphates only. The liquids derived from beef and horse-flesh yield a mixture of alkaline phosphate (of potash and soda), which gives a yellow precipitate with salts of silver, and of pyrophosphate of soda and potash, which produce a white precipitate. The flesh of fowl yields pure pyrophosphates.

The relation between the potash and soda salts in the liquids of the flesh and in the blood differs considerably; to 1 equiv. of potash the blood of an ox contains 12 to 13 equivs. of soda; this relation is reversed in the aqueous extract of the flesh of the same animal. The blood of the horse contains to 1 equiv. of potash 3·62 equivs. of soda; with the same quantity of soda the flesh of the same horse contains 6·9 equivs. of potash. These relations will lead to some important conclusions, if we bear in mind that the salts of potash predominate in the milk. If a soda salt (a phosphate of soda) is requisite for the constitution of the blood of many animals, it follows that the addition of chloride of sodium to the food of these animals is likewise necessary and indispensable for all those districts where the forage does not contain phosphate of soda or soda salts, which is the case in many parts of Germany. It is easily conceived that the chloride of sodium by reciprocal decomposition with phosphate of potash (which predominates in our cerealia) is able to furnish phosphate of soda and chloride of potassium, and this latter salt is never wanting in the liquids of the flesh.

In conclusion, I may add, that creatine, by long-continued boiling with very concentrated barytic water, is decomposed into urea (or into carbonate of baryta and ammonia), into a new organic base, which forms with sulphuric acid a salt crystallizing in nacreous laminæ, resembling chlorate of potash, and into a new crystalline acid, which I have not been able to investigate from want of material.—*Comptes Rendus*, Jan. 18, 1847.

Silicate of Soda in the Blood of Fowls.

M. Henneberg has found that the blood of fowls contains silicate of soda (or of potash), a fact which explains the existence of the enormous quantity of silica which has been stated to occur in their feathers.

On the Amides. *By* M. Malaguti.

When 1 part of oxamide is boiled with 4 parts of nitric acid of 1·35 spec. grav., a gas is given off which consists of 1 vol. nitrogen, 1 vol. nitrous oxide, and 2 vols. carbonic acid; the same happens therefore in this case as when 1 equiv. nitrate of ammonia and 1 equiv. oxalic acid are boiled together; the oxygen of the nitric acid oxidizes not only the hydrogen of the ammonia, but likewise the carbon of the oxalic acid. When crystallized oxalate of ammonia is exposed in a closed vessel to a temperature of 428° F., it is converted, without the formation of any oxamide, into carbonate of ammonia and carbonic oxide.

When oxamide is heated to 590° in a hermetically-closed metallic tube, it is converted, in the course of a few minutes, into cyanogen, carbonic oxide and carbonate of ammonia ($C^2H^2NO^2 = Cy + 2HO$). On heating a mixture of sand and oxamide in a tube from 572°–626°, there is likewise obtained only carbonate of ammonia, cyanogen and carbonic oxide.

The chloracetate of ammonia yields, when heated according to the former experiments of the author, phosgene gas, chloride of ammonium and carbonic oxide. When chloracetamide is decomposed at a faint red heat, a large quantity of gas is obtained, which contains much carbonic acid, gaseous chloride of cyanogen, carbonic oxide and some phosgene gas,

$$(C^4Cl^3O^2H^2N = CyCl + Cl^2H^2 + C^2O^2).$$

This decomposition may be somewhat modified by several circumstances. When chloracetamide is heated with water in a closed glass tube above 212°, chloroform and carbonate of ammonia are formed without the chloracetamide being previously converted into chloracetate of ammonia; if the tube be opened when the temperature has attained to 266°, the chloracetamide is found unaltered, while chloracetate of ammonia is already decomposed between 234° to 239° into chloroform and carbonate of ammonia.

The author likewise investigated the decomposition of mucamide by heat. Mucic æther is immediately converted, by contact with liquid ammonia, into mucamide, a white substance, which is very soluble in boiling water, and is deposited in microscopic needles on cooling. It is void of taste, insoluble in alcohol and æther; its spec. grav. at 56° = 1·589. It is converted, under the influence of water at 277°–284°, into mucate of ammonia. Its formula is $C^6H^6O^6N$; a boiling solution of it yields with ammoniacal acetate of lead a precipitate of ammoniacal acetate of lead, $C^{12}H^8O^{14}$, 2PbO, H^3N + 6HO. Treated with sulphuretted hydrogen, it yields sulphuret of lead and bimucate of ammonia. A saturated boiling solution of mucamide produces in an ammoniacal solution of nitrate of silver a brilliant mirror of silver. When mucate of ammonia is heated to 428°, it becomes soft and coloured, disengages carbonic acid, water, carbonate of ammonia, pyromucic acid and a peculiar amide, and leaves a residue of carbon and paracyanogen. When mucamide is heated to 392°, it becomes brown, disengages at 406° much water, softens and melts at 428°, evolving the same amide as on heating the mucate of ammonia, some pyromucic acid, carbonic acid and carbonate of ammonia; at 464° the decomposition is complete; the residue consists of carbon and paracyanogen. Of these products, the carbon, paracyanogen and water constitute the most considerable,

$$C^{12}H^{12}N^2O^{12} = C^4N^2 + C^8 + 12HO;$$

while on heating mucate of ammonia, paramucic acid, the peculiar amide, carbonate of ammonia, carbonic acid and water preponderate. The last decomposition is rather complex; and it is possible that, assuming the mucate of ammonia to be decomposed into pyromucic

acid, carbonate of ammonia and water, the two first form, by their reciprocal action, the amide, together with carbonic acid and water. According to this view, the decomposition of the mucate of ammonia would be as simple as that of the mucamide. The amide (*pyromucamide biamidée*), which is obtained in the destructive distillation of the mucate of ammonia or of the mucamide, dissolves but sparingly in water, and may therefore be readily purified by recrystallization from adherent pyromucic acid. It tastes like sugar, dissolves in alcohol and æther, but sparingly in cold water, and disengages ammonia only when boiled with the fixed alkalies. It melts at 347°, becoming coloured and partially decomposed, and boils at 500°. Its formula is $C^{10}\,H^{3}\,O^{2}$, $2H^{3}\,N$. Pyromucamide differs essentially from this body; its taste is scarcely sweet; it dissolves in alcohol, æther and water, and melts at 266°–269°, becoming green, then blue, violet, and finally black. The portion which distils over is brown, but it may be completely decolorized by animal charcoal. The formula of this body is $C^{10}\,H^{6}\,NO^{4}$.

It frequently happens, in the preparation of the mucic æther, that the impure aqueous solution suddenly disengages a very distinct odour of alcohol, becomes acid, and yields on evaporation a residue which is different from that of mucic æther. This substance is purified, by frequent treatment with alcohol, from the intermixed mucic æther; it is then dissolved in water, and crystallized twice or three times. The substance is pure when its solution is no longer rendered turbid by ammonia. The body thus obtained is white, resembling asbestos in appearance, and crystallizing in minute prisms whose base is a parallelogram; it is tolerably soluble in water, but very sparingly so in alcohol; has an acid taste, melts at 374°, assuming a vitreous appearance; but after being left for some time, the mass again becomes opake and soft. It is represented by the formula $C^{16}\,H^{14}\,O^{16} = C^{6}\,H^{4}\,O^{7}$, $C^{4}\,H^{5}\,O$, $C^{6}\,H^{5}\,O^{8}$. 1 equiv. of this *mucovinic acid*, exposed to a current of dry ammoniacal gas, absorbed 1 equiv. ammonia with evolution of heat. The salt thus formed, $C^{16}\,H^{14}\,O^{16}$, NH^{3}, is readily soluble, tasteless, and of a faint acid reaction. Its solution precipitates salts of silver, lead, copper, baryta, strontia, some of lime, and not those of zinc, magnesia, &c. All these precipitates are soluble in acetic acid. When a solution of mucovinic acid is boiled with oxide of silver, a portion of the oxide is reduced with disengagement of carbonic acid; while a combination is formed with silver, which readily explodes on the application of heat.—*Comptes Rendus*, xxii. p. 851.

On a new Salt of Zinc. *By* Dr. J. Allan.

This salt is prepared by adding a considerable quantity of alcohol to an alkaline solution of chloride of zinc in ammonia, when, after some time, the liquid deposits groups of perfectly white crystals, which when dry have a nacreous lustre. The crystals are likewise very easily obtained by adding æther to the liquid until it begins to be turbid. On analysis they yielded—

	Found.	Calculated.
Chlorine	13·59	14·15
Ammonium	6·53	7·19
Oxide of zinc	66·56	64·27
Water	13·32	14·39

leading to the formula $ClNH^4 + 4(ZnO + HO)$.—Liebig's *Annalen*, October 1846.

Milk-Sugar in the Milk of Dogs.

Dr. Bensch has found the milk of three dogs, fed on meat for 12, 15 and 27 days, to contain milk-sugar, which may be easily obtained in a perfectly crystalline state.

PATENT.

Patent granted to Peter Ward, Oldbury, Worcester, *for Improvements in the Manufacture of certain Salts of Soda and Magnesia.*

It is well known to those engaged in the manufacture of soda ash, that, after the liquor or lyes from the black ash has been evaporated or salted down, the ash thus obtained contains a large quantity of caustic soda and sulphuret of sodium. To render this ash fit for making soda crystals, it is desirable to convert the caustic soda into carbonate of soda, and the sulphuret of sodium into sulphate, or sulphate of soda; and for this purpose it is usual to mix sawdust with the ash, either during the operation of salting it down in the furnace, or after that it has been drawn therefrom and previous to its being introduced into the carbonating furnace.

This mixture of ash and sawdust, when brought into the carbonating furnace, is worked in the usual way, with a slow fire at first to burn off the sawdust; the fire is then increased sufficiently to communicate to the ash a red heat, and maintained until the ash is in a proper state to be used for making crystals of soda.

During this process it is found that, whilst the sawdust is in a state of combustion, the caustic soda and sulphuret of sodium are fused and form small globules, which retard the process of carbonating, and the conversion of the sulphuret of sodium into sulphate, or sulphate of soda. It is also a matter of experience that the caustic alkali dissolves a portion of the sawdust or carbonaceous matter, and gives to the alkaline solutions a greenish or dark colour, that is, if the ash be drawn from the carbonating furnace before the action of the fire has fully removed the colouring matter.

In consequence of the difficulty experienced in getting rid of the colouring matter in the carbonating furnace, it is useful to employ a solution of the chloride of lime, in order fully to remove this greenish or dark tint from the alkaline liquors previously to making use of them in the manufacture of crystals of soda.

In order to obviate these difficulties, which occur in the process just mentioned, and to obtain a more perfect carbonate of soda, the patentee takes carbonate of magnesia in the state of fine powder, in the proportion of from 3 to 7 per cent. of the dry ash, according to the quantity of caustic soda and sulphuret of sodium which may be present in the ash operated upon; and mixes this proportion of such carbonate of magnesia with the alkaline liquors when they are being boiled down to the state of ash in the salting-down furnace, or with the ash after it has been drawn from that furnace, and previously to its being introduced into the carbonating furnace.

The ash thus mixed with the carbonate of magnesia is put into the ordinary carbonating furnace, and submitted to the usual treatment for about 3 hours for 700 cwt. of ash. The advantages derived from the use of carbonate of magnesia in this operation are twofold. In the first place, the carbonate of magnesia, being infusible at the greatest temperature required in this operation, has the effect of keeping the mass of ash in a porous and open state, thereby greatly facilitating the conversion of the sulphuret of sodium into sulphite or sulphate of soda, and the caustic soda into carbonate of soda. In the second place, the carbonate of magnesia being subjected to a red heat, as is the case in this process, gives out carbonic acid, which, uniting with the caustic soda, forms carbonate of soda. The ash, when taken from the carbonating furnace, is dissolved in water; the magnesia subsides, and carries down with it any oxide of iron that may be present in the solution of the carbonate of soda, and leaves the liquor in a fit state for making crystals of soda. If, on examination, the liquor derived from the ash be not clear and free from colour, it shows that the ash did not remain sufficiently long under the influence of the fire in the carbonating furnace to produce the above effect.

The magnesia thus precipitated is separated from the liquor, and, after being washed with water to remove the alkaline liquor fully from it, is allowed to settle in a tank; and when taken from the tank it may be dried and used to advantage, in the same manner as the carbonate of magnesia, as above described in the manufacture of soda-ash; or else it may be transferred into suitable vessels of stone or lead, where sulphuric acid and water may be added in such proportions as will produce a saturated solution of sulphate of magnesia of about the specific gravity 1·165. The patentee prefers making use of sulphuric acid of the specific gravity 1·750, in order that it may, when mixed with water, produce sufficient heat to dissolve readily the magnesia.

The saturated solution of sulphate of magnesia thus obtained is pumped into another vessel, and enough sulphuret of magnesium added to precipitate any iron which is present in the state of sulphate of iron; by this addition of sulphuret of magnesium, sulphuret of iron and sulphate of magnesia are formed.

Sulphuret of calcium may be used in this process to supply the place of sulphuret of magnesium; in this case, sulphuret of iron and sulphate of lime will be the salts formed. It is necessary to use the

sulphuret of calcium cautiously; for should it be added in excess, it will decompose the sulphate of magnesia*.

The sulphuret of calcium, which may be made available in the foregoing process, is prepared from vat-waste, an oxysulphuret of calcium produced during the decomposition of the sulphate of soda in the manufacture of soda-ash. It may be obtained in a state fit for use by pouring hot water on the vat-waste, and allowing it to remain about 6 hours in the vat, and then running it off. When the sulphuret of iron has subsided, the clear liquor is drawn off, and conveyed into a leaden pan, and boiled until it acquires the usual specific gravity; it is afterwards run into crystallizing vessels, and finished in the usual manner. If, after the separation of the sulphuret of iron from the liquor as above mentioned, it is found to contain any colouring matter derived from the sulphuric acid or any other source, a clear liquor may be obtained by mixing a small quantity of chloride of lime in solution to the liquor previous to boiling it preparatory to crystallization.

The sulphuret of magnesium is prepared as follows:—60 parts by weight of the dry sulphate of magnesia and 40 parts by weight of coke, finely powdered, are introduced into a common iron retort, which is then subjected to the action of fire until the whole mass shall have been maintained at a red heat for about 6 hours. The contents of the retort are afterwards taken out, and when cold dissolved in hot water. The liquor thus obtained, being separated from the insoluble impurities, is then fit for use.

Heretofore Epsom salts have been manufactured from magnesian limestone, which requires to be calcined and washed, in order to separate the carbonate of magnesia; the patentee found that in some cases, native carbonate of magnesia is found in a state of purity, or else so slightly mixed that it may be considered pure for the purposes of his invention, part of which consists in employing native carbonates of magnesia in the manufacture of Epsom salts, without subjecting them to calcination and washing; the native carbonates of magnesia which the author employs are imported from Greece; and when native carbonate of magnesia is employed, without calcining and washing, for the manufacture of Epsom salts, it is either applied first in the manufacture of carbonate of soda, as above explained, or else the native ore put into a vessel, and sulphuric acid poured upon it, and then treated in a manner similar to that used for converting the magnesia, after its separation from the soda-ash, into Epsom salts or sulphate of magnesia.—Sealed July 6, 1846.

* It is necessary, in order fully to precipitate the iron, to add sulphuret of magnesium or calcium until a black precipitate ceases to take place.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Cyanic Acid upon Alcohol and Aldehyde. *By* J. Liebig *and* F. Wöhler.

Allophanic Acid.—The authors formerly described, under the name of cyanic æther, a body which is instantly formed when the vapour of cyanic acid is passed into alcohol. It crystallizes in colourless prisms, and is decomposed at an elevated temperature into alcohol and cyanuric acid. Its composition was found on analysis to be represented by the empirical formula $C^8 N^2 H^8 O^6$, which may be regarded as a combination of 1 equiv. æther, 2 equivs. cyanic acid, and 3 equivs. water; or, simplifying the formula, as a combination of 3 equivs. æther, 2 equivs. cyanuric acid, and 3 equivs. water; it might also be viewed as a combination of 3 equivs. alcohol with 2 equivs. cyanuric acid, in accordance with its mode of decomposition by heat. Whether we assume this body to contain cyanic or cyanuric acid, it does not possess a composition analogous to that of the other æther compounds, since it is decomposed by barytic water, forming a baryta salt which neither behaves like the cyanate nor the cyanurate of baryta, but belongs to a new acid, *allophanic acid*. This acid contains the elements of 2 equivs. cyanic acid and 3 equivs. water; its composition is expressed by the formula $C^4 N^2 H^3 O^5$. The crystallized cyanic æther is the perfectly normal anhydrous æther compound, and consists of 1 equiv. æther $= C^4 H^5 O$, and 1 equiv. allophanic acid $= C^4 N^2 H^3 O^5$. It is formed by 2 equivs. hydrated cyanic acid, assimilating the atom of water which separates from the alcohol on its conversion into æther. In proof of this view is the fact, that this acid may be transferred to other bases.

Allophanate of baryta ($BaO + C^4 N^2 H^3 O^5$) is formed when the æthyle or methyle compound is dissolved in barytic water; it separates gradually in hard warty agglomerations of crystals, alcohol, which can be separated with all its properties, being left in the liquid. The best plan is to triturate the æther with barytic water and crystallized hydrate of baryta, when the former gradually dissolves entirely, and the excess of hydrate of baryta remains undis-

solved; no heat must be employed in this operation. The liquid is then filtered into a stoppered vessel, and set aside well-closed for several days; the baryta salt gradually separates, generally in isolated, transparent, round aggregations of minute crystals; and sometimes in adherent crystalline crusts. On decanting the liquid, a minute quantity of carbonate of baryta, which may have been accidentally deposited, is washed away, and the crystals then rinsed once or twice with a little cold water, and allowed to dry at the ordinary temperature. The salt has an alkaline reaction, and dissolves entirely, although with difficulty, in water; when its solution is heated, it becomes turbid even below 212°, and deposits the entire amount of baryta as carbonate; at the same time carbonic acid is given off with effervescence, and only urea is to be found in the liquid. When the salt is heated in a retort, it disengages a large amount of carbonate of ammonia ($NH^3\ CO^2$) without the slightest trace of water, and is converted into neutral cyanate of baryta, which fuses to a clear mass. When the salt is treated with an acid, it disengages carbonic acid without the least odour of cyanic acid; the solution formed contains not a trace of ammonia, as would be the case with the cyanate, but only urea. It is even decomposed in the same manner, only more slowly, by carbonic acid. When macerated with a cold solution of carbonate of ammonia, carbonate of baryta and urea are the sole products. The solution of the barytes salt is rendered turbid by neutral acetate of lead only after the lapse of half an hour, but the precipitate is pure carbonate of lead. When the barytes salt is triturated at the ordinary temperature with a solution of a little sulphate of soda, the corresponding soda salt is formed; it is obtained in minute prisms when the solution filtered from the sulphate of baryta is mixed with alcohol. Its solution has an alkaline reaction, and is not precipitated by chloride of barium; but if it be heated, it immediately deposits carbonate of baryta. If allowed to evaporate *in vacuo*, the salt is left as an amorphous gelatinous mass, with a bluish iridescence. Evaporated between 104° and 122°, it yields a mixture of unaltered salt, carbonate of soda and urea, which latter may be extracted by alcohol. If nitric acid be mixed with a solution of the soda salt, carbonic acid is evolved, and soon afterwards bright scales of nitrate of urea separate.

The soda and potash salt may also be obtained crystallized by dissolving the cyanic æther in an alcoholic solution of hydrate of soda or potash. The potash salt very soon separates in laminæ which closely resemble those of the chlorate of potash. The lime salt also crystallizes, is very difficult of solution, and is obtained by dissolving the cyanic æther in lime water, and allowing the liquid to stand in a tightly-closed bottle. All these properties exhibited by the salts accord with the view that it is a peculiar acid $= C^4N^2H^3O^5$, and are not to be explained with probability in any other manner. This acid, when separated from its base in the presence of water, or when the solution of its salts is heated, assimilates the elements of 1 atom water, and is decomposed into carbonic acid and urea. The analysis of the barytic salt yielded—

Carbon.....	13·80	13·30	4	14·01
Hydrogen	1·89	..	3	1·74
Nitrogen	15·01	15·87	2	16·33
Oxygen	23·99	..	5	23·35
Baryta.....	45·31	44·00	1	44·57

The equivalent weight of allophanic acid is 1188·04; it is constituted as if it were a combination of 2 equivs. carbonic acid, 1 equiv. cyanic acid and 1 equiv. ammonia; when 1 equiv. water is added, the two latter form urea, and the carbonic acid is evolved. It is unnecessary to state that the crystallized body which is formed by the action of cyanic acid upon wood-spirit is the methyle compound of allophanic acid.

Trigenic Acid.—The mode of origin of allophanic acid induced the authors to examine the action of cyanic acid upon aldehyde. The reaction is highly remarkable; the two bodies form with one another a new acid, which is called trigenic acid. Its composition in the crystallized state is expressed by the formula $HO + C^8 N^3 H^6 O^3$; it may be regarded as a combination of 2 equivs. cyanic acid, 1 equiv. aldehyde and 1 equiv. ammonia. Including the basic atom of water, it contains the elements of 1 atom urea and 1 atom of cyanate of aldehyde; it originates from 1 equiv. aldehyde ($C^4 H^3 O + HO$), and 3 equivs. hydrated cyanic acid, the elements of 1 equiv. cyanic acid with the basic water of all 3 equivs. of cyanic acid being converted into carbonic acid and ammonia. The ammonia enters into the compound; carbonic acid is evolved as gas; the atom of water of the aldehyde becomes the basic water of the acid.

Trigenic acid is prepared by passing the vapour of cyanic acid into anhydrous aldehyde; the vessel in which it is contained is placed in cold water. A few grammes only can be used at once, while otherwise explosive ebullitions occur, by which the mass is projected in all directions. The liquid becomes warm, and after a short time suddenly boils violently, owing to the evolution of carbonic acid, and is converted into one mass of froth; this finally congeals to a tenacious vesicular mass, exactly like calcined borax. If the aldehyde has been cooled by ice, which is undoubtedly the best plan, it mixes with the acid without acting upon it, and only when the mixture attains the temperature of the air does the evolution of carbonic acid begin, which then may continue for hours and days like a fermenting liquid. The product forms either a tenacious semisolid mass or a syrupy yellowish liquid, in which gradually crystalline crusts are formed. Besides trigenic acid, it contains cyamelide, aldehyde-ammonia, and probably other collateral products. It is dissolved in moderately strong muriatic acid, boiled so long as vapour of aldehyde is given off, and filtered hot; on cooling, most of the trigenic acid crystallizes in minute prisms. It is generally somewhat yellowish, but is readily obtained perfectly colourless by dissolving it in boiling water and treating it with a little animal charcoal; the acid then crystallizes in minute radiately-grouped prisms; it has an acid reaction and a faint acid taste, and dissolves with difficulty in water, and scarcely at all in alcohol. It melts

when heated, is decomposed and carbonized, giving off a vapour which smells strongly of quinoline and has an alkaline reaction. This property is very characteristic, and deserving of particular attention as being a new mode of forming quinoline. The acid was distilled from a small retort, when at first a product was obtained which solidified to a soft yellowish mass, smelled strongly of quinoline, had an acrid taste and an alkaline reaction; finally, vapour of cyanic acid passed over. The first product was redistilled with dilute solution of caustic potash, when immediately with the water quinoline began to pass over in colourless oily drops; on the addition of a little muriatic acid they dissolved, and the strong odour disappeared entirely. This solution gave with chloride of platinum a crystalline double salt, which disengaged with caustic potash the odour of quinoline. The solution of potash from which the quinoline had been distilled deposited, after saturation with muriatic acid, a quantity of minute crystals, which were cyanuric acid. This is probably formed at a certain period of the decomposition from cyanic acid and ammonia, *i. e.* from urea, which may possibly also be contained in the products of distillation, just as it is found among those of uric acid.

To prepare the silver salt of trigenic acid, a solution of the acid is precipitated by neutral nitrate of silver and dilute ammonia. The salt separates as a white powder, and contains no ammonia; by exposure to light it becomes violet. It is seen under the microscope to consist of transparent spherical agglomerations of crystals. It dissolves in hot water, from which it is likewise deposited on cooling in a pulverulent form. Between 248° and 266° it parts with water and becomes of a pure light brown; somewhat above 320° it melts instantly, becoming black and giving off a dense vapour, which smells strongly of quinoline. Analysis yielded—

Carbon	37·78	38·26	38·42	8	37·24
Hydrogen	5·81	5·94	6·07	6	5·41
Nitrogen.....	32·24	..	..	3	32·54
Oxygen	24·17	..	..	4	24·81

Deducting the atom of water which is replaced in the silver salt by 1 equiv. oxide of silver, gives 1501·02 for the atomic weight, and supposes in the silver salt 49·12 per cent. oxide of silver. Cyanic acid appears to exert a perfectly similar action upon acetone as upon alcohol and aldehyde.—Liebig's *Annalen*, lix. p. 291.

On the Pre-existence of an Essential Oil in Starch.
By M. Payen.

Many years ago the author asserted the pre-existence of an essential oil in starch, which was denied by most chemists, and especially by Liebig. In proof of the correctness of his view, he now brings forward the following experiments:—500 grms. of starch were gradually added to 3 litres of boiling water, which had been acidified with 0·005 sulphuric acid, contained in a vessel capable of holding 6 litres; the condensation was effected in an apparatus similar to

that which the author has described in the separation of the aroma from coffee*. About half a litre of water condensed in the first two recipients; in the third, towards the end of the operation, some cubic centimetres of water; and in the fourth, which was surrounded by ice, only a few drops. The water in the first two recipients possessed the odour of the starch, and was covered with a whitish pellicle, which dissolved in æther and solidified on cooling. The water of the third recipient had a very strong odour of starch, and was covered with a layer of essential oil; by uniting the collected essential oil the author obtained 0·08 grm. of it. It was liquid, yellowish, had a very strong odour of starch, and at all events a lower boiling-point than that of water. The water poured from the oil still yielded 0·018 of oil; so that the starch contains at least 0·0001 part by weight of essential oil.—*Comptes Rendus*, xxiii. p. 487.

Research on the Juice of the Aloe. By E. Robiquet.

In a memoir of considerable length, the author first enters upon the consideration of the structure of the leaves of the aloe, and then describes the chemical properties of the juice. Of the first part we shall confine ourselves to a brief notice. The epidermis of the leaves has no stomata; between it and the leaf parenchyma a number of air-ducts occur, which were for a long time considered to be milk-sap vessels. The sap flows in the intercellular passages between these vessels, and forms an acid colourless liquid, in which a number of transparent bodies are suspended, and which give to it a somewhat milky appearance. On the access of air the juice absorbs oxygen with great rapidity, and acquires a yellowish colour, which gradually becomes darker. The outer portions of the parenchyma consist of a regular cellular tissue; the inner ones, on the contrary, of regular broad cells, which are filled with a mucilaginous acid juice, which acquires a violet colour on exposure to the air. In this almost pasty mass numerous symmetrically distributed air-bubbles are perceptible; and in the outer portions numerous rhaphides, consisting of sulphate of lime.

The chemical experiments were made with that kind of aloes which Robiquet had obtained under the name of the now scarce Socotrine aloes. It had been received from England, and consisted of small masses, each weighing 100 grms.; these were transparent, and possessed a yellow dark garnet-red surface; their smell resembled that of myrrh and ipecacuanha. The surface of fracture is lighter towards the centre, sometimes of an amber-yellow colour. If some thin fragments be examined with a lens, minute golden yellow points are perceptible upon a more or less pale garnet-red ground. This aloes softens at 172° F., and melts at a somewhat higher temperature; it dissolves entirely in alcohol, but only slightly in æther; water extracts $\frac{1}{3}\frac{1}{6}$th of its weight; it does not however yield a clear solution, but only a turbid liquid, in which numerous minute yellowish bodies are suspended; when, however,

* See page 36 of the present volume.

the aqueous solution is exposed to the air, it becomes perfectly clear in the course of a few days; subsequently it becomes dark yellow, and after some months of a splendid purple-red. If the liquid be now evaporated, a dark red, almost black residue remains. Robiquet convinced himself that this colour was produced by the absorption of oxygen, and that the commercial aloes owes its dark colour to the same cause. Owing to the change which the aloes experiences from the action of the atmospheric oxygen, it becomes somewhat more soluble in cold water, and acquires the property of colouring silk of a beautiful aventurine-red. Persalts of iron produce in the solution a black precipitate, which indicates the presence of gallic acid in the commercial aloes, but this also appears to pre-exist in the plant. Perchloride of gold yields with a dilute solution a pulverulent precipitate, which entirely possesses the colour of gold-purple, and consists of pure gold. This circumstance speaks in favour of the view of those chemists who regard gold-purple as consisting of pure gold in a finely-divided state, and the tin in it only as an impurity.

If aloes be mixed with cold muriatic acid of moderate strength, the former seems to experience no essential change; but if the temperature be raised, the liquid quickly becomes brown, and disengages a gas of the odour of burnt caoutchouc, which when washed with solution of potash proved to be a mixture of carbonic oxide and carburetted hydrogen. When the liquid was boiled until no more gas was given off, twice its volume of cold water was added to it, when a brown loose powder subsided, which, after being well washed with water and dried, proved to be ulmic acid. The brown filtered liquid was evaporated in the water-bath to expel the excess of acid, and mixed with 5 to 6 times its volume of cold water, when an orange-coloured flocculent precipitate separated, which, collected on a filter and washed, possessed all the properties of purified aloes. The ulmic acid does not appear to have been produced solely by the action of the muriatic acid, for much more of it is obtained from old aloes, which has experienced considerable change from exposure to the air, than from fresh samples; moreover, muriatic acid does not form the least trace of ulmic acid, even on long-continued boiling with purified aloes.

Forty years ago Braconnot examined the products of dry distillation of aloes; his experiments, however, were not made with Socotrine aloes. The author heated 60 grms. of powdered Socotrine aloes in a tubulated retort gradually to 500° in an oil-bath. The products were—

	Grammes.
Water, with essential oil	14
Acid water	8
Empyreumatic oil	10
Carbonaceous residue	28
Sulphate, phosphate, carbonate of lime, carbonate of potash	traces

The milky odoriferous water which passes over between 167° and

230° owes its properties to a colourless neutral essential oil, which is lighter than water, but which, on account of its small quantity, could not be further examined. The acid liquid is a mixture of water and acetic acid. The heavy black oil does not differ from that obtained in the dry distillation of wood. No trace of ammonia could be detected; the pure aloes appear therefore to contain no nitrogen.

Aloes contains a tolerable quantity of foreign constituents, which render its purification difficult. The sample examined by the author consisted of—

Pure aloes	85·00
Ulmate of potash	2·00
Sulphate of lime	2·00
Carbonate of potash, Carbonate of lime, Phosphate of lime	traces
Gallic acid	0·25
Albumen	8·00

To separate the pure substance, the pounded aloes was exhausted with cold water, the liquid evaporated to half its volume, and treated with an excess of acetate of lead; a light yellow flocculent precipitate was formed, consisting of gallate and ulmate of lead, together with albuminate of lead and traces of carbonate and sulphate of lead. On adding a sufficient quantity of ammonia to the filtered liquid, the precipitated oxide of lead carried down the greater portion with it. The orange-coloured precipitate, which soon became of a greenish-yellow by exposure to the sun's light, was decomposed with sulphuretted hydrogen, access of air being prevented. The liquid filtered from the sulphuret of lead was perfectly colourless, and gave on evaporation no crystals, but a yellowish residue resembling a varnish, which the author calls *aloetine*. This aloetine dissolves readily in water and in alcohol, sparingly in æther, and not at all in fatty or volatile oils. When heated to redness, it yields a shining, bulky cinder, which is finally burnt without residue; it gives no precipitate with persalts of iron or with acetate of lead, and behaves in other respects like the solution of the aloes itself. When the experiments have been made with access of air, the mass obtained is not colourless, but dark red; but in its other properties it exactly resembles the first.

Aloetine possesses in a high degree the purgative properties and the bitterness of the common aloes. In a therapeutic respect, 8 parts of aloetine represent 10 parts of Socotrine and 50 parts of Cape aloes. The resinates of potash and lime, which Peretti stated he had discovered in the Cape aloes, are nothing further than ulmate of potash with carbonate of lime and some unaltered aloes, and his three pigments consist of more or less altered aloetine. In fact, when a solution of aloetine is exposed to the air, it finally passes through brown into a purple-red; now if such a liquid be evaporated precisely when it possesses a distinctly brown or red colour, the residue may be regarded as a distinct colouring substance. The elementary analysis of aloetine yielded 27·69 per cent. C, 10·77 H,

and 61·54 O, which would correspond to the formula $C^6 H^{14} O^{10}$, which however must only be regarded as approximative.

In the treatment of aloes with nitric acid, the author obtained the chrysammic and chrysolepic acids discovered by Schunck. The chrysammic acid forms, when mixed with ammonia, bichrysammate of ammonia, $2(C^{15} H^2 N^2 O^{13}) NH^3$, which is converted in the cold into chrysammamate of ammonia $(C^{30} H^6 N^5 O^{25}) NH^3$. The latter parts with its ammonia at 212°, so that chrysammamic acid is left, which by the action of very dilute sulphuric or nitric acid parts with 1 equiv. ammonia and 1 equiv. water, so that chrysammalide, $C^{30} H^2 N^4 O^{24}$, is obtained. By long boiling with water the latter is again converted into chrysammamic acid, which finally can be restored by alkalies or strong acids to the state of chrysammic acid. To prove these metamorphoses, however, with certainty, a far greater number of analyses will be necessary. The polychromic acid, which Boutin obtained by treating aloes with nitric acid, is, according to the author, only a mixture of resinified aloes with chrysammic acid; for if it be washed with small quantities of æther, this extracts the resinified aloes; while the residue, when saturated with carbonate of potash and crystallized from boiling water, yields distinct crystals of chrysammate of potash. Boutin's *cyanile* is, according to the author, nothing further than a mixture of formic and hydrocyanic acids. In the distillation of a mixture of nitric acid and aloes, the author always observed a very strong odour of oil of bitter almonds, formic acid and oil of Spiræa. On saturating the acid liquid, the odour of the latter was alone perceptible; when the distillation is continued, the odour of oil of bitter almonds and of formic acid prevail, while that of the hydruret of salicyle disappears. In the first period of the distillation the nitric acid acts consentaneously upon all the constituents of the ordinary aloes; in the second period the aloetine is already changed, and the nitric acid acts merely upon the impurities; the formation of the hydruret of salicyle consequently ceases, a small quantity of prussic acid and carbonic acid pass over, and the residue consists in great part of oxalic acid.

[To be continued.]

Observations on Zircon. By W. Henneberg.

As is well known, the coloured zircon loses its colour by exposure to heat; but this change is also accompanied by other peculiar phænomena. At a temperature which does not raise a thin platinum crucible to a dark red heat, the zircon crystals heated in it exhibit a phosphorescence which rapidly extends on all sides from the parts most heated and soon ceases. Some crystals always diffuse a stronger light than others, and have then become perfectly colourless and transparent; others diffuse a much less powerful light, and retain their colour; but they are rendered colourless by the heat of the blowpipe flame. A mineral which has once exhibited this phænomenon of incandescence does not so any more when again heated. Previous to ignition the crystals possessed the specific gravity 4·615,

and after ignition 4·710; the condensation therefore is as 10000 to 9798.

In an analysis made by the author, the mineral was decomposed with carbonate of soda with the addition of one-eighth nitre, which is very advantageous in many cases, especially with mica. The separation of the peroxide of iron from the zirconia was effected by passing sulphurous acid into the mixture of hydrated zirconia and sulphuret of iron, precipitated by ammonia and sulphuretted hydrogen, until the precipitate is decolorized. The iron dissolves along with a small quantity of zirconia, which however is thrown down on boiling in combination with sulphuric acid and potash. If only carbonate of soda has been employed, a portion of the earth remains in solution after boiling, as sulphate of soda does not form a sparingly soluble double salt with it, and it is then precipitated along with the peroxide of iron. The zirconia obtained is perfectly free from iron. The analysed mineral contained 33·85 per cent. SiO^3, 64·81 Zr^2O^3, with traces of KO, 1·55 Fe^2O^3, and 0·88 CaO = 101·09. The formula $Zr^2O^3 + SiO^3$ requires 33·68 per cent. SiO^3, and 66·32 Zr^2O^3.—*Journ. für Prakt. Chem.*, xxxviii. p. 508.

Experimental Researches on the Nutritive Power of dry and fresh Fodder. By M. Boussingault.

It is generally thought that green fodder is more nourishing than the hay obtained from an equal weight of fresh grass. The experiments of the author show that this is not the case. A heifer was weighed, and fed for ten days on green fodder; each day a quantity equal in weight to that consumed was put aside to dry. The animal was again weighed, and fed for ten days on the dry fodder, then weighed again. The experiment was repeated three times, and each time the animal weighed a little more after feeding on the dry fodder than after the green. The difference was not enough to prove that the dry food was the more nutritious, although the experiments showed beyond a doubt that it was not inferior in effect to the other.—*Ann. de Chim. et de Phys.*, xvii. p. 291.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Uric Acid. By W. Heintz.

Lehmann found that uric acid, dissolved in solution of potash, was completely precipitated from it by acetic acid. But since, according to Liebig, the uric acid in the urine is held in solution by phosphate of soda, the author considered further experiments requisite to ascertain whether the usual method of determining uric acid would likewise yield sufficiently accurate results in the present case. In order to determine, in the first place, the solubility of uric acid in water, the author dissolved 0·1485 grm. of uric acid in 65 grms. of a very dilute solution of phosphate of soda, precipitated

then with muriatic acid, &c., and obtained 0·1425 grm. uric acid; consequently the loss does not amount to more than 0·006 grm. In a second experiment, the author obtained from 0·3028 grm. uric acid, which was dissolved in 80 grms. of a dilute solution of phosphate of soda, 0·2966 grm. uric acid; the difference in this case amounts therefore to 0·0062 grm. In a third experiment the loss was 0·0058. This unavoidable loss in the determination of uric acid is evidently so inconsiderable, that it cannot give rise to any very great errors.

The author now sought to ascertain in how far the colouring substances, which are generally precipitated with the uric acid, may increase its weight. For this purpose a weighed quantity of uric acid was heated with a concentrated solution of phosphate of soda, and then mixed with boiling urine, which had been previously freed from uric acid by treatment with muriatic acid and 24 hours' rest. In the first experiment the excess amounted to 0·0085 grm.; the loss occasioned by washing must have been very inconsiderable, and the addition of acid water could not have given rise to any error. If we suppose 0·0015 grm. as uric acid which had been dissolved in the washing, the colouring substance precipitated with the uric acid would be 0·01 or 0·1 part in 1000 of the liquid employed (98 grms.). In a second experiment an excess of 0·0051 was found; the quantity, therefore, of the colouring substance precipitated by the muriatic acid about compensates for the loss occasioned by washing the uric acid.

The next point to determine was, whether perhaps certain normal constituents have any influence upon the value of this mode of determination. The author found that *grape-sugar* has not the slightest influence. In the experiments with the solution of albumen acetic acid was used instead of the muriatic acid, and the mixture digested for some time at 122°, in order to decompose the whole of the urate and to avoid any possible coagulation of the albumen. In the first experiment there was a loss of 0·0033 grm. uric acid, or 0·05 part in a thousand of the liquid; in a second, 0·006 grm. uric acid, or 0·08 part in a thousand of the liquid; in the third, 0·0085 grm. uric acid, or 0·09 part in a thousand of the liquid; and in the fourth, 0·003 grm. uric acid, or 0·05 part in a thousand of the liquid. It is evident, from these experiments, that the presence of albumen in the urine does not interfere with the determination of the uric acid when in its precipitation acetic acid is used. When *blood* is contained in the urine, the uric acid must be likewise precipitated with acetic, and not by muriatic acid. The method which the author followed in these experiments was identical with the preceding, only instead of the solution of albumen the liquid was substituted which had been obtained by extracting the clot of blood with cold water and filtration. The loss of uric acid found in one experiment was 0·0003 grm.; in a second experiment there was an excess of 0·0044 grm.; but in both cases the uric acid was coloured brown by the pigment which had been precipitated along with it, especially in the second experiment. On employing, in a third experiment, phosphoric

instead of acetic acid, the precipitated acid was scarcely coloured; the loss amounted to 0·0028 grm., or 0·04 part in a thousand of the liquid employed. This latter, in the first experiment, had become, upon the addition of acetic acid, somewhat brownish; in the second, perfectly dark brown and opalescent; while in the third it still retained the beautiful red colour upon the addition of the phosphoric acid, but became somewhat darker. The degree of this change of colour depends upon the quantity of acid employed; and it is therefore requisite, in order to avoid as much as possible the simultaneous precipitation of the colouring substance of the blood by the acid, to add only so much acetic or phosphoric acid that the liquid possesses a strong acid reaction, but to avoid too large an excess. With respect to the presence of blood, therefore, the error occasioned by it is so small, that it can have no essential influence upon the quantitative determination of the uric acid.

Although it is extremely improbable that all the constituents of the bile should occur, nevertheless the author made some experiments with a solution of bile which had been freed from mucus by some acetic acid. In the first two experiments acetic acid was employed to precipitate the uric acid; in the last two, muriatic acid. In the first experiment the loss amounted to 0·0146 grm., or 0·22 part in a thousand of the liquid; in the second, 0·0174 grm. uric acid, or 0·25 part in a thousand of the liquid; in the third, 0·0159 grm. uric acid, or 0·24 part in a thousand of the liquid; and in the fourth, 0·0110 grm. uric acid, or 0·18 part in a thousand of the liquid. The differences, therefore, which are occasioned by the presence of bile are considerably higher than in all the cases previously mentioned; but probably in an icteric urine the error would not be so great, because the quantity of the bile is very inconsiderable. Müller's *Archiv für Anat. und Physiologie*, 1846, p. 383.

On a new Method of estimating Nitric Acid. *By* M. Gossart.

The examination of the oxidizing action of nitre under the influence of sulphuric acid has proved to me that, in a great number of cases, the products of this action may be rendered constant, and so furnish a large number of processes for the accurate estimation of nitric acid and the nitrates. In the following method I have been guided by the principle applied by M. Pelouze to the estimation of copper. In analysing crude nitre I employ as reagents,—1st, an acid solution of the protosulphate of iron*; 2nd, a very dilute solution of the red ferrocyanide of potassium.

I pour into a flask with a long neck 50 cubic centimetres of sulphuric acid of 1·704 spec. grav., and 25 of a solution of saltpetre containing 10 grms. of refined saltpetre in a demilitre; I then add, with a graduated burette, some drops of the solution of the protosulphate of iron, and agitate gently; the mixture becomes brown, suddenly clears again, and acquires a more or less deep straw colour.

* The solution of the protosulphate which I have usually employed was strongly acid and nearly saturated.

I then continue to add in drops a normal solution, the strength of which I wished to ascertain, waiting each time until the liquid brightens; when these changes of colour become less rapid, I apply a gentle heat; and when they are no longer perceptible, I examine whether, on taking a few drops with a pipette, they still yield a blue colour with the red ferrocyanide of potassium. When this blue colour appears, and no longer disappears on boiling the liquid, I note down the total number of the divisions employed. A second examination, in which a large number of the trials may be dispensed with, will yield an accurate result.

Let N be the number of divisions of the normal solution requisite to saturate completely 25 cubic centimetres of the solution of refined nitre; I weigh off 10 grms. of the saltpetre to be examined, which I likewise dissolve in a demilitre of water, and determine, in the same manner as was done for the solution of refined saltpetre, the number N^1 of divisions of the protosulphate of iron required to saturate completely 25 cubic centimetres of this solution; and the fraction $\frac{N^1}{N}$ gives the strength of the saltpetre under examination with great accuracy.

This process, which is applicable to the estimation of nitric acid, and of all the nitrates in general, may be employed for determining the quantity of nitric acid contained in gun-cotton. For this purpose, the whole of the cotton is oxidized with a mixture of sulphuric acid and peroxide of manganese; the liquid is filtered, and decolorized with a few drops of protosulphate of iron, which decomposes the whole of the sesquioxide of manganese before acting upon the nitric acid. In this manner a solution is obtained containing the whole of the nitric acid which existed in the pyroxyline, and the amount of which may be readily estimated.—*Comptes Rendus*, Jan. 4, 1847.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Examination of Water for Towns, for its Hardness, and for the Incrustation it deposits on boiling. By Professor Clark*

At various times during the last few years, I have been applied to for information respecting methods I had adopted for examining waters for towns; but ill health has almost always prevented me from returning a satisfactory answer. There has been recently somewhat more occasion for such inquiries, in consequence of the Commissioners of Woods and Forests having been pleased to require, as one of the indispensable conditions to a bill for supplying water to a town being presented by them to Parliament, that there shall be given, in reference to the waters already supplied to the town, as well as in reference to the waters proposed to be supplied,—

* From a private circular addressed by Prof. Clark to his chemical friends.

"A statement of the quality of the water as exhibited by chemical analysis, specifying its adaptation for domestic and manufacturing purposes, and its degree of hardness with reference to the tests and scale of Dr. Clark."

I take the liberty to write out one answer to all inquirers; and, imperfect as I am aware the information must be, I hope my friends will receive it with such indulgence as is due to an effort at affording information to others by a person confined to bed by illness and unfit for any considerable exertion of mind.

The processes alluded to for the examination of waters are two—one for ascertaining the hardness of water, one for ascertaining the alkalinity.

Each of these processes is fully described in the specification of a patent printed in the Number of the 'Repertory of Patent Inventions' for October 1841.

A water is indeed most materially affected in its fitness for domestic uses and manufacturing purposes by the degree of its hardness. But many hard waters have the additional objection of depositing earthy matter on being boiled. This matter forms an incrustation on the boiler, and fills up tubes employed in giving passage to the heated water. In this land of steam-engines it need not be told how annoying this quality is. Not only should the chemist be able to tell, ay or no, whether any such deposit will be formed; but, when one does occur, it is desirable to know how much altogether, and how much of each of the more important kinds of matter will be deposited. Now, in the specification alluded to, there is no express direction given for obtaining this important point of information, because this was not necessary to the invention there described; neither indeed had I then contrived a method for the purpose. But ever since September 1845 I have been accustomed to derive this information from the hardness and the alkalinity of the water boiled and unboiled. To explain the method of deducing this information is a principal object of the present note.

Referring to the specification, I begin by describing a few improvements that have been suggested by experience since the specification was enrolled.

Process for ascertaining the Hardness of Water.

In June 1843, having occasionally before met with some few specimens of waters, and more especially soft waters from springs, where the indications of the soap-test, which in general are remarkably distinct, were obscure, I discovered the cause of this obscurity to be an excess of carbonic acid, that is, an excess over and above what is necessary to form alkaline or earthy bicarbonates. This excess has the property of slowly decomposing a lather once formed.

For the purpose of guarding against an excess of carbonic acid in all cases, I recommend that, before you measure out the water for trial, you shake it briskly in a stoppered glass bottle half-filled with it, sucking out the air from the bottle at intervals by means of a glass tube, so as to change the atmosphere in the bottle.

In all trials of waters above 16° hardness, not only should such waters, and the distilled water to be used along with them in the trials, be treated in this manner, previous to their being measured out and mixed, but the measured mixtures themselves should be treated in like manner, before any soap-test is added to them. The soap-test itself should be occasionally so treated before it is measured out.

To obtain uniform results with the soap-test, I recommend that as soon as you observe that a lather is formed, such as will remain all over the surface of the water for five minutes, you take a note, but only an *interim* one, of the quantity of the soap-test that has been added. In about half an hour you should shake the bottle again, to see whether the lather will still remain for five minutes. If the water under trial do not exceed 4° or 5° of hardness, it is likely to require a little more soap-test upon this renewed shaking; but in every case where more soap-test is required, let more be added to the water. This latter quantity and the former will together make up the whole soap-test that is to determine the hardness of the water under trial. For hours afterwards, unless perhaps the water do not exceed 1° or 2° of hardness, a lather lasting for five minutes may be restored by your shaking the phial. This mode of procedure, by producing a lather whose permanence we may repeatedly verify, will conduce much to the uniformity and accuracy of our trials.

Table for converting Soap-test Measures into Degrees of Hardness.

Ever since detecting the fallacy that might occur owing to an excess of carbonic acid, my health has prevented me from performing such a series of experiments as to afford materials for a table of this kind. Pressed, however, by the present occasion, and guided by my former experience, I have endeavoured to frame, as follows, a table worthy of confidence, by comparing together unpublished results obtained since then by others.

Table of the Soap-test Measures, corresponding to 100 *Test Measures of each Standard Solution.*

Degree of Hardness.	Soap-test Measures.	Differences for the next 1° of Hardness.
0 (distilled water)	1·4	1·8
1	3·2	2·2
2	5·4	2·2
3	7·6	2·0
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	1·9
8	17·5	1·9
9	19·4	1·9
10	21·3	1·8
11	23·1	1·8

Degree of Hardness.	Soap-test Measures.	Differences for the next 1° of Hardness.
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·7
16	32·0	

When the measures of soap-test necessary to form a lather, with 100 test-measures of a water, exactly correspond with a standard solution, then the degree of hardness will be the corresponding integral number found in the first column. Thus 24·9 of soap-test will indicate 12° of hardness; 26·7 of soap-test will indicate 13° of hardness.

But if the measures of soap-test do not exactly correspond with a number in the first column, the hardness will be expressed partly by an integer and partly by a fraction.

The *integer* will be the hardness corresponding to the next lower number in the soap-test column.

The *numerator* of the fraction will be the excess of the soap-test measures in question above this number. The *denominator* of the fraction will be the corresponding difference which follows the soap-test in the next column.

Example.—Let 25·8 be the measures of soap-test required by 100 test-measures of a given water.

24·9 is the next lower number in the soap-test column. Therefore 12° of hardness, the corresponding degree, is *the integral part* of the required hardness.

The numerator of the fraction is 25·8 − 24·9 = 0·9. The denominator is the corresponding difference = 1·8. *The fraction* itself is $\frac{0{\cdot}9}{1{\cdot}8} = 0{\cdot}5$.

The whole hardness therefore is 12°·5.

Process for ascertaining the Alkalinity of a Water.

The tests employed are two,—test-paper and the acid test. Respecting these I have little to add to what is given in the specification.

Test-paper.—The colour should be first separated from the solid matter of the litmus by boiling, subsidence, filtration, &c. The coloured solution thus obtained being too weak for use, will require to be concentrated by evaporation. The colour will then have to be brought to a proper tint by means of dilute nitric acid, and afterwards applied to the paper by a flat camel-hair brush. The only paper that I have found to be sufficiently free from acid or alkaline impurities to be unexceptionable for test-paper, is the drawing-paper stamped with the name of Harding.

Acid Test.—In purifying oxalic acid, it is desirable to reject a very small crop, consisting of such of the crystals as fall first. These, I find, contain quadroxalate of potash. I find a little of this salt, even when the acid has been made by means of pure (?) nitric acid

and specimens of the best refined sugar of commerce—a circumstance well worthy of the attention of chemists engaged in the study vegetation.

Degrees of Hardness and Degrees of Alkalinity explained.

Degrees of Hardness.—Each degree of hardness indicates as much hardness as would be produced by 1 gr. of chalk per gallon, held in solution in the form of bicarbonate of lime, free from any excess of carbonic acid. The degree of hardness caused by a lime salt depends, not on the state of combination of the calcium it contains, but on the quantity of the calcium. If, instead of being in the form of bicarbonate of lime, the calcium this compound contains were in the form of chloride of calcium, or of nitrate of lime, or of sulphate of lime, or even of lime-water, the soap-test destroyed by it, and consequently the degree of hardness indicated, would be precisely the same.

A quantity of a soluble magnesian salt equivalent to 1 gr. of chalk, destroys a like quantity of soap-test, and consequently indicates one degree of hardness. The same is the case with salts of iron and salts of alumina. Salts of the alkalies do not produce hardness.

Degrees of Alkalinity.—For each degree of alkalinity that a water possesses, a gallon of it will require as much acid to neutralise it as 1 gr. of chalk would require. Hence a solution of lime-water, or of bicarbonate of lime, in distilled water should be of the same degree of hardness as of alkalinity. The most usual cause of alkalinity in water is bicarbonate of lime; but bicarbonate of magnesia, which causes hardness, likewise causes alkalinity; and bicarbonate either of soda or of potash, which does not cause hardness, causes alkalinity *.

To infer the Degrees of Hardness and the Degrees of Alkalinity from an ordinary Analysis.

For Hardness.—Compute the grains of lime, magnesia, oxides of iron, and alumina, in a gallon of the water, each into its equivalent of chalk. The sum of those equivalents will be the hardness of the water.

For Alkalinity.—Compute in like manner the grains of bicarbonates of lime, magnesia, soda, and potash, in a gallon of the water, each into its equivalent of chalk. The sum of those equivalents will be the alkalinity of the water. But the results thus obtained have much less chance to be accurate than the hardness and the alkalinity ascertained directly by means of the soap-test and the acid-test.

Delicacy of the Tests.

For Hardness.—Suppose the Thames water to yield a mean of 14° of hardness. Carefully conducted experiments should then range between 14°·1 and 13°·9 of hardness. That is to say, the mean result

* When a phosphate of lime is present, as happens rarely and in small quantities, it is probable that for every two degrees of hardness the phosphate occasions it will produce only one degree of alkalinity; that is, all the lime in the phosphate will cause hardness; but one half of it will be neutralized, and only the remaining half alkaline.

of more experiments than one should be within 0°·1 of the extremes; and it is to be remembered that the hardness of a water may be ascertained repeatedly within an hour. But 0°·1 of hardness is equivalent to one-tenth of a grain of chalk per gallon; that is, 1 of chalk in 700000 times its weight of water. But as the operation is performed on only the 70th of a gallon (1000 grs.), the whole weight of hardening matter that we actually operate upon in this experiment is a 70th of 14 grs., that is, one-fifth of a grain; and the smallest weight to which we actually measure is the 70th of the 10th of a grain, that is, the 700th of a grain. I do not remember any process of equal quantitative delicacy in the whole range of chemical analysis; and this one is the more remarkable as it is performed with soap-test, previously known as almost the rudest and least determinate of chemical reagents.

For Alkalinity.—If the Thames be at 14° of hardness, it would probably yield 13°·1 of alkalinity. Such a water, if tried according to the directions of the specification, should give 13°·1 of alkalinity each time. The difference between the experiments, if carefully performed, should appear not on the first, but only on the second place of decimals. Now since 1° of alkalinity corresponds to 1 gr. of chalk per gallon, and since the acid-test indicates less than 0°·1 of alkalinity, or 1 of chalk in 700,000 of water, we may safely infer that the acid-test will measure 1 of chalk in 1,000,000 of water. Thus we obtain for record even more accurate results by the acid-test than we do by the soap-test. Nevertheless the soap-test is, in the abstract, the most delicate, for although we use nearly the same quantity of each test, yet in the case of the acid-test we act on the 8th of a gallon, whereas in the case of the soap-test we act on only the 70th of a gallon.

How to make the foregoing Processes available for ascertaining the Quantity of Incrustation the Water deposits on boiling.

For this purpose the points to be ascertained are,—

1. The hardness and the alkalinity of a given water, unboiled.

2. The like particulars of the same water, after being boiled, without loss of steam, for at least 2½ hours, and then cooled, and (if necessary) filtered.

From these indications, the weight per gallon of earthy deposit formed by boiling, if there be any, is deduced as follows:—

Let h = hardness of unboiled.
Let h' = hardness of boiled.
Let $h - h' = H$, that is, degrees of hardness lost by boiling, occasioned by the precipitation of earthy salts, which may be either alkaline or neutral, or partly both.

Let a = alkalinity of unboiled.
Let a' = alkalinity of boiled.
Let $a - a' = A$, that is, degrees of alkalinity lost by boiling, occasioned by the precipitation of alkaline earthy salts.

Note.—Observe that H is equal to A only in the case where *all* the precipitate is chalk and carbonate of magnesia, which is but seldom the case.

$H - A =$ so much of the hardness lost by boiling as is produced by the precipitation of neutral earthy salts.

$(H - A) \times 1{\cdot}36 = B$, that is, the above neutral earthy salts, calculated as dried sulphate of lime, in grains per gallon.

Collected and represented in a report thus :—

Hardness of the water { Unboiled ..... Boiled .....

Deposit by boiling, in grains, per gallon :—

Alkaline earthy salts, calculated as chalk ..... A

Neutral earthy salts, calculated as dried sulphate of lime B

Total ..... $A + B$

Alkalinity of the water { Unboiled..... Boiled.....

When the alkalinity is only 1° or 2°, it is not worth while boiling the water, as hardly any precipitation will take place.

If you cannot conveniently arrange so as to boil the water without loss of steam, I recommend that you boil it with as little loss as possible, and, when the water has cooled, that you make up the loss in weight of the vessel and its contents by adding distilled water. Mere boiling causes one change in the saline contents of the water. Boiling with evaporation causes an additional change.

I recommend that the alkalinity of a water be always stated by itself in a report, that is, not mixed up with the hardness; perhaps indeed it should be given in the Appendix to the Report, for persons not familiar with chemistry are apt to be puzzled about the alkalinity, whereas the degree of hardness and weight of deposit per gallon scarcely ever give them any difficulty. But the alkalinity should not be altogether omitted from the Report, as the statement of it is necessary for a comparison of the results obtained by different chemists.

It will be for others to decide whether the ascertaining of the quantity of the deposit that a water forms on boiling should or should not form a part of the chemical analysis serving to specify "its adaptation for domestic and manufacturing purposes," as required by the Commissioners of Woods and Forests.

T. C.

2 Argyle Place, Rothsay, Isle of Bute, 20th February 1847.

On the Production of Boracic Acid in Tuscany.
By M. Larderel.

The basins in which the boracic acid is found in solution are called lagoons. When the soil exhibits at any spot a high temperature, and vapours of sulphur ascend from it, or any earthquake is felt, a basin, more or less deep according to the locality, is dug there,

A column of vapour suddenly issues with considerable force from the earth; this is surrounded with a wooden chimney, in order to protect the workmen. A suitable form is given to the basin and the sides lined with stone. The depth and circumference of such a basin must be in a certain relation to the force of the column of vapour; for instance, when the depth and surface are too great, and the basin consequently contains too much water, so that the vapour encounters great opposition, it frequently happens that it seeks another passage. These eruptions of vapour, however, are not very constant, and sometimes cease without any blame attaching to the workmen. Frequently indeed the volcano, after several years' regular activity, disappears, and seeks a new passage at a distance of from 30 to 60 metres. From the inconstancy of these eruptions, the localities are dangerous to visit without a safe guide. There is no knowing, when the eruption ceases at a certain spot, where it will break out anew; it then frequently forms a subterranean lake near the surface, which the weight of a man passing easily breaks, to meet with a very dangerous scalding. Such accidents are of frequent occurrence.

As soon as the walls of the lagoon are finished, the chimney is removed, and water from some source conducted into the basin, where it is heated to boiling by the ascending vapour. In the vicinity of the lagoons a distinct odour of sulphuretted hydrogen is perceptible. The water, of which not much is evaporated, takes up from 1 to $1\frac{1}{2}$, rarely 2 per cent. boracic acid. The lagoons are emptied every day, as the amount of boracic acid is not increased by remaining there longer; and the solution is conducted from one basin into another, so that when it reaches the reservoir to clarify, it is of a homogeneous nature. In this reservoir the water deposits the mud, &c. suspended in it, and which, as it contains no more boracic acid, is not further exhausted, but removed from time to time. As soon as the water is become clear, it is conducted into the evaporating pan, which is heated with the volcanic steam. After 62 hours' concentration it is conveyed into wooden cooling vessels, where it is left three days to cool and deposit crystals of boracic acid. The motherley is poured back into the clarifying reservoir, and the crystals of boracic acid dried in chambers heated by volcanic vapour. The dimensions of the lagoons differ considerably; the smaller ones are about 100 feet in circumference and 7 feet deep, but there are some which are from 500 to 1000 feet in circumference, and 15 to 20 feet deep. There are generally several, from 3 to 15, sources in the latter. The construction of these basins required considerable works; terraces had to be built and hollows filled up, in order to keep the water at the suitable level; rivulets had to be turned out of their course, to prevent their injurious influence upon the basin.

To heat the evaporating pans, &c., those sources are turned to account which are not suited for the construction of lagoons. The jets are surrounded in the manner above described, and thence conveyed in subterranean stone passages beneath the evaporating pans. Each series consists of 14, 18, and even 26 pans, 1 foot in depth and 10 feet superficies. The vapour condensed in the passages flows off

through an aperture, the uncondensed escapes through a chimney. The formation of boracic acid is not yet explained, although several hypotheses have been advanced on the subject; the vapour as it rushes forth from the soil contains no boracic acid, for when it is condensed and evaporated not a trace is found in the residue, nor does the soil in the vicinity of the sources contain any; but it is formed after the vapours have been in contact with a certain quantity of water.

With respect to the history of the production of boracic acid in Tuscany, Peter Höffer discovered the boracic acid in the lagoons of the Monte Rotondo, in the year 1777, in the reign of Duke Leopold the First. Two years later Prof. Mascagni took up this observation, but it was only in 1818 that the sources were turned to account by the author for the production of boracic acid. The first experiments were made on Monte Cerboli, whence originated the establishment which was called Larderello after the author. Soon after this two other works were erected, the one near Lustignano, the other on the Monte Rotondo. From the success which these works met with, the number has now increased to ten,—Monte Cerboli (Larderello), Castel Nuovo, Lasso, Monte Rotondo, San Frederigo, Lugo, Sant Ippolyto, Lustignano, Acquaviva, Serrazzano; the first three are situated in the district of Pomerance, the others in that of Massa Maritima. At present there are 400 evaporating pans in operation, each of 10 feet surface, besides which there are several evaporating pans, with diaphragms arranged in rows, 300 feet in length, in which the water constantly evaporating, flows slowly through the different divisions, until at last it is so concentrated that it may be conveyed at once into the cooling vessels. More than 1200 lbs. of water are evaporated in the course of a day. Until 1827 wood was employed for heating the evaporating pans, which increased the expenses of production so much that but little was produced; since which time, however, the author has introduced the above-described method of heating by steam, by which a saving of about 10,000,000 francs has been effected. The production of boracic acid has increased in the following proportions:—

	Pounds, Tuscan weight.
1818–1828.....	1,500,000
1829–1838.....	14,000,000
1839	2,152,000
1840	2,525,752
1841	2,547,804
1842	2,655,139
1843	2,655,202
1844	2,655,200
1845	2,655,000

The production this year (1846) will amount to 3,000,000 lbs. of boracic acid; it may be still further increased if required.—*Comptes Rendus*, xxiii. p. 345.

THE CHEMICAL GAZETTE.

No. CVI.—March 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Behaviour of Metallic Zinc towards Solutions of Mercury. *By* H. Rose*.

The behaviour of metallic zinc towards solutions of the peroxide and perchloride of mercury is highly remarkable. The zinc throws down the whole of the mercury from solutions of the pernitrate and persulphate, when the separation of basic salts has been prevented by the addition of nitric or sulphuric acid. The zinc does not combine with the mercury, but the latter separates in the form of gray globules, which collect at the bottom of the vessel; the zinc retains its appearance, becoming only somewhat more gray than before the experiment.

Zinc behaves in the same manner towards a solution of the perchloride of mercury; its appearance is not changed, and the mercury separates in gray globules; but when hydrochloric acid has been added to the solution of the perchloride, the immersed bar of zinc soon becomes quite bright and shining. In this reaction no evolution of gas occurs; only a few bubbles adhere constantly to the bright surface of the amalgamated metal; the mercury is only imperfectly precipitated, for even after several days its presence may be detected in the solution. It is true that, when the zinc is left for a longer time in contact with the liquid, the mercury is at last entirely separated, but not however as a precipitate of gray globules; but the whole of it combines with the zinc and amalgamates it. At all events, when free hydrochloric acid is present, the mercury is separated far more slowly, and under totally different phænomena, than from the solution of the pure perchloride.

When the experiment is somewhat modified, the result is still more surprising. For instance, if a bar of zinc be immersed in hydrochloric acid, and when the evolution of hydrogen is very rapid, a solution of perchloride of mercury be added, the disengagement of gas ceases instantly; the zinc becomes bright, resulting from its amalgamation; and after several days the mercury is only imperfectly separated from the solution. If a solution of perchloride of platinum be now added, evolution of hydrogen immediately recommences.

* Communicated by the Author.

When the mercury has been entirely separated from a solution of the perchloride by zinc in the form of gray globules, and hydrochloric acid added, the zinc soon becomes bright and amalgamated, without however the mercury, which has been separated in the form of globules, wholly combining with the zinc.

The behaviour of amalgamated zinc is very remarkable. Döbereiner observed that no evolution of gas resulted on the contact of amalgamated zinc with acids; and recently Millon has drawn attention to the fact, that certain metallic solutions hasten the evolution of hydrogen by means of zinc and dilute sulphuric acid (a phænomenon which has been satisfactorily accounted for by Barreswil), while a solution of perchloride of mercury retards this disengagement considerably.

Zinc, as is well known, is most readily amalgamated by immersing it in hydrochloric acid, and then rubbing it over with mercury. Zinc thus amalgamated remains perfectly bright when placed in hydrochloric acid, in which it scarcely dissolves at all, or so little, that only a few bubbles of gas adhere to the shining surface. As is well known, amalgamated zinc behaves, in an electrical point of view, almost like a distinct metal; and, notwithstanding it is but little acted upon by acids, is more positive than zinc alone. If, therefore, another metal be placed by the side of amalgamated zinc, which is in contact with a dilute acid, a powerful evolution of gas immediately results on the former when it touches the amalgamated zinc. It is requisite, however, that, in order to retain its remarkable behaviour, especially towards perchloride of mercury, there must always be some free acid present, without which it acts like ordinary zinc. When an amalgamated bar of zinc is immersed in a solution of perchloride of mercury, the mercury is separated exactly as with pure zinc in the form of gray globules, and the amalgamated zinc loses its bright coating. In the same way amalgamated zinc reduces solutions of the sulphate of copper, nitrate of silver and acetate of lead, like ordinary zinc, with this difference, that an addition of hydrochloric or nitric acid does not prevent or retard the reduction of the metals by the amalgamated zinc, as is the case with the solution of perchloride of mercury.

When only a few drops of hydrochloric acid are added to a solution of the perchloride of mercury, the zinc is amalgamated; but after some time mercury separates in the form of gray globules, which does not occur when a larger quantity of hydrochloric acid has been employed.

Dilute sulphuric acid acts like hydrochloric acid in preventing or retarding the precipitation of the mercury from the solution of the perchloride; frequently, in this case, a fine crystalline salt separates, which however is only perchloride of mercury, which is far less soluble in dilute sulphuric acid than in water; subsequently a crystalline powder separates in minute scales, coating the zinc, and frequently floating upon the surface of the liquid; this is the protochloride of mercury, which is not further altered by the zinc. It is remarkable that the protochloride is only separated by zinc from the

solution of the perchloride when sulphuric acid has been added, and not from a solution of the pure chloride, nor on the addition of hydrochloric acid. Moreover, when a solution of the perchloride of mercury is poured upon zinc immersed in dilute sulphuric acid, the evolution of gas suddenly ceases, just as with the addition of hydrochloric acid. The zinc likewise becomes amalgamated, and a few bubbles of gas adhere for a long time to its surface. Nitric acid also prevents the precipitation of the mercury from the solution of the perchloride by zinc, in the same manner as hydrochloric and sulphuric acids; in this case the protochloride is also formed. When a violent disengagement of nitric oxide has resulted from immersing zinc in nitric acid, it is instantly stopped by the addition of a solution of the perchloride of mercury. It is well known that neither sulphuric nor nitric acids in the dilute, and also in the concentrated state, are capable of decomposing the perchloride of mercury.

Iron completely precipitates the oxysalts of mercury in the same manner as zinc; the metal is likewise wholly separated by iron from a solution of the perchloride, and an addition of hydrochloric acid neither prevents the evolution of gas nor the elimination of the mercury; as the iron is not amalgamated, the mercury separates in the form of globules.

While zinc entirely precipitates the mercury from a solution of the protonitrate, it cannot decompose the protochloride even when recently precipitated and in the presence of water. The insolubility of the salt is by no means the cause of this phænomenon, as the chloride of silver is most quickly and rapidly decomposed by zinc in the presence of water. Even on the addition of hydrochloric acid, the protochloride is not decomposed by zinc, or only to a very small extent when it has been left for several days in contact with it and the acid. Scarcely any evolution of gas is perceptible in this instance; nevertheless the liquid, after a short time, contains oxide of zinc in solution.

The insoluble protosulphate of mercury is likewise not reduced by zinc in contact with water; however, after several days some oxide of zinc has dissolved, and the zinc is slightly amalgamated; more is reduced when dilute sulphuric acid is added, but still the quantity is very inconsiderable; there is no evolution of gas, but nevertheless the zinc is amalgamated.

On the Action of Nitric Acid upon Brucine. *By* A. Laurent.

It had been stated by Gerhardt, that nitrous æther was formed in the action of nitric acid upon brucine, when this, as is well known, is coloured red, an assertion which Liebig declares to be unfounded. Laurent, who repeated Gerhardt's experiment, arrived at the same result, but obtained moreover a new substance, which he calls *cacotheline*, the composition of which is represented by the formula $C^{21}H^{22}N^4O^{10}$. This substance yields, on treatment with ammonia, various products, one of which is a powerful base.—*Comptes Rendus*, xxii. p. 633.

Researches in Animal Chemistry. By Prof. Liebig. *In a Letter to* M. Gay-Lussac.

The following facts will serve to complete my former communication*:—The first, and in my opinion the most curious, is the existence of lactic acid in the fluids of the muscles of the Carnivora. I have obtained a quantity of lactic acid from a wild fox equal at least to that found in an ox; and from another fox, which had been confined and fed for 200 days upon meat only, I procured a quantity not less considerable.

I have investigated the decomposition which creatine experiences under the influence of barytic water; in my former communication I mentioned the formation of a new acid as a product of the decomposition of creatine, but I subsequently discovered that it is an accidental product. By continual ebullition with barytic water, creatine is decomposed into urea and a new organic base; the urea is in its turn converted into ammonia and into carbonate [of baryta], which is deposited in minute but very distinct crystals. If we subtract the elements of urea from the composition of creatine, we obtain precisely the formula of the new base.

The formula for creatine is	$C^8 N^3 H^{11} O^6$
subtracting from which urea	$C^2 N^2 H^4 O^2$
leaves	$C^6 N H^7 O^4$

which is the formula found by the analysis of the base itself and its sulphates; it expresses the quantity which combines with 1 equiv. of oxide, and shows that this base is isomeric with the lactamide discovered by M. Pelouze.

The new base is very soluble in water. When this solution is in a syrupy state, it deposits, on spontaneous evaporation, very brilliant large crystals, which possess the same crystalline form as the sulphate of magnesia; they are insoluble in alcohol and in æther. This base is very volatile; it sublimes at a temperature lower than that of boiling water. Owing to this property, which I was not able to foresee, a considerable loss of this precious substance occurred in its preparation.

The composition of the new nitrogenous acid, the barytic salt of which I noticed in my preceding communication, is expressed by the formula $C^{10} N^2 H^6 O^{10}$; it contains therefore in 1 equiv. the same number of atoms of carbon as uric acid. I fear I shall not be able, from want of material, to analyse and study the other nitrogenous acid, which is found in the liquids of the flesh, and consequently in the broth. Both possess the taste of broth, and diffuse, upon heating their salts upon platinum, the odour of roast meat. The salt of potash, and all the soluble salts of the first acid, precipitate entirely salts of copper; a white precipitate, of the appearance of the hydrate of alumina, is obtained with nitrate of silver; it also precipitates salts of lead. All the salts of this acid are insoluble in alcohol, even in weak spirit. The soluble salts of the other acid

* See page 81 of the present volume.

have no action upon the salts of copper, silver and lead; they dissolve in weak alcohol, from which they may be crystallized. The alkaline salts of these two acids yield after calcination a mixture of cyanide of potassium and cyanate of potash.—*Comptes Rendus*, Feb. 8, 1847.

On a new Series of Acids of Sulphur. By E. Plessy.

In a previous memoir* I described two acids produced by the action of sulphur and chlorine combined upon sulphurous acid in the presence of water. In continuing my investigations on this subject, I have been led to the discovery of a new series of acids of sulphur. I first endeavoured to make myself better acquainted with the acid resulting from the decomposition of the protochloride of sulphur; after having verified the accuracy of my former analyses, I questioned whether the formula which I had adopted could be retained; evidently not unless my acid and the acid S^4O^5 should present different properties; now both these acids yield, under the same circumstances, the same products of decomposition.

The bisulphated hyposulphate of baryta, $S^4O^5BaO, 2HO$, prepared by the process of MM. Fordos and Gelis, was left to itself in a concentrated solution. The salt was decomposed; and among the products, which according to those chemists are sulphur, sulphurous and sulphuric acid, I found a considerable quantity of a body which had escaped their attention; it is the acid of M. Langlois. We have $S^4O^5MO = S^3O^5MO + S$. The acid, therefore, obtained with the protochloride of sulphur is identical with the bisulphated hyposulphuric acid (S^4O^5); it exhibits, however, towards certain tests different reactions, owing probably to MM. Fordos and Gelis not having obtained their salt perfectly free from that of M. Langlois. The observations which I have made upon the acid S^4O^5 have been of great assistance to me in the examination of the products of decomposition of the perchloride of sulphur.

Action of Sulphurous Acid on the Perchloride of Sulphur† *in Presence of Water.*—The salt $S^5O^6BaO, 2HO$, which I formerly described, parts with sulphur on solution in water, and gives origin to a new salt, which, after having been dissolved in water and precipitated by alcohol several times, leaves on calcination 50·48 per cent. sulphate of baryta; when dried *in vacuo* it leaves a greater residue, viz. 52·42 per cent. The following is the composition of the salt dried *in vacuo*:—

Sulphur	36·24
Base	34·48
Water and oxygen	29·28

These numbers lead to the formula S^5O^7BaO, HO; and for the salt which has not been dried, $S^5O^7BaO\,2HO$.

I have ascertained that the salt $S^5O^6BaO\,2HO$ contains two acids,

* Chem. Gaz., vol. iii. p. 405.

† Obtained by passing an excess of chlorine into the protochloride.

one of which being more sulphated than the acid $S^5 O^7$, is capable of yielding this acid on parting with sulphur. I have not been able to isolate this most sulphated acid, but have nevertheless been able to deduce its formula from my observations; it is $S^6 O^7$. The formation of the acid $S^5 O^7$ compels us to admit the existence of the acid $S^6 O^7$; we have, as with the bisulphated hyposulphuric acid, $S^6 O^7 MO = S^5 O^7 MO + S$.—*Comptes Rendus*, Feb. 8, 1846.

Research on the Juice of the Aloe. By E. Robiquet.

[Continued from p. 96]

Caustic lime has a very remarkable action upon aloes. The author triturated 100 grms. aloes and 50 grms. burnt lime together, passed the mixture through a fine hair-sieve, and heated it in a retort until white vapours began to be disengaged; the fire was then removed, and the reaction left to proceed of itself. This is very violent; the apparatus is filled with white vapours, and disengages combustible gases in considerable quantity; when the recipient is well cooled, an oily product is obtained. However, no further heat should be employed to hasten the reaction; for this would then be so violent that the apparatus would burst. When the disengagement of vapours and gases has ceased, the liquid distils quietly over; the temperature may now be very cautiously increased, but only so that drop follows drop, until it may finally be raised to a red heat. The recipient is then changed and the firing increased, when similar products are obtained as in the dry distillation of aloes. As the *aloisole* formed by the distillation of aloes with lime is produced only in small quantity, it is requisite, in order to obtain a sufficient quantity for examination, to repeat the operation several times, and to unite the products. After standing for 12 hours the liquid separates into two layers; the first consists of impure acid aloisole, the under one of an acid water. Sometimes we likewise find at the bottom of the vessel some drops of a yellowish-green non-volatile oil, which has been carried over in the distillation. The aloisole is removed with a pipette, and shaken with barytic water until all trace of acid reaction has disappeared; the separated oil is then dried in closed tubes with chloride of calcium for some days, in order to avoid oxidation. To obtain the oil perfectly pure, it is again distilled once or twice in the oil-bath, and only that which passes over at 266° collected. Since aloisole absorbs oxygen from the atmosphere with great avidity, only the first third of the distillate can be used for analysis; the other portion can be employed for studying the products of decomposition. The tubes in which the product is preserved must be sealed and protected from the light of the sun. 100 parts of aloes do not yield more than 1 part of pure aloisole.

Pure aloisole is a colourless or pale yellow liquid, and possesses a penetrating odour which calls to mind that of potato fusel oil and of oil of bitter almonds. It is perfectly insoluble in water, but dissolves in every proportion in alcohol and æther; at 266° it boils;

at 59° its specific gravity is 0·877; it does not solidify even at 4°. In a chemical point of view it behaves like an aldehyde, becoming acid very readily in contact with the air; dry ammoniacal gas is rapidly absorbed by it in the cold, forming with it an oily liquid, which dissolves in alcohol, but is insoluble in water and æther. This can only be obtained undecomposed below 32°, and is decomposed under other circumstances into aloisole and ammonia. If to the compound some cold sulphuric acid is added, no remarkable reaction is perceptible; but as soon as the mixture is warmed a considerable quantity of aloisole is separated. It sufficed, in order to obtain the above ammonia-compound, to pass a current of dry ammoniacal gas through an æthereal solution of aloisole, which is kept cool by a freezing mixture; an oily liquid soon subsides to the bottom, which can only be preserved with great cold and under considerable pressure. The author found it impossible to determine the quantity of ammonia absorbed, as the product was decomposed too rapidly.

If an alcoholic solution of aloisole be heated in a glass tube with some ammonia and nitrate of silver, the sides of the tube become coated with metallic silver, which, according to the quantities employed, exhibits a more or less bluish reflexion, depending apparently upon the great tenuity of the silver mirror. No compound isomeric with aloisole could be prepared from it, nor could a hydrate be obtained. Exposed to the air, aloisole very soon becomes brownish-red from the absorption of oxygen, and is converted into an acid which is somewhat heavier than water, and which the author has called *aloïsic acid*. This oxidation may very easily be rendered perceptible, by placing at the bottom of a vessel some caustic potash, moistening this with some æther, and then pouring upon it a layer of water, which the potash cannot absorb until the æther has been displaced. Now if some aloisole be let fall upon the water, upon the surface of which it remains, it is very soon converted by oxidation into aloïsic acid, which sinks in red streaks through the liquid, but immediately disappears when it reaches the solution of potash.

To ascertain the action of chromic acid upon aloisole, the author placed 2 to 3 grms. of it in a small pipette, bent its two drawn-out ends parallel, and broke off the points. The pipette was now thrown into a small retort filled with a solution of 10 grms. of chromic acid in 30 grms. of water; the neck of the retort was drawn out and bent at a right angle, and fitted into a glass tube, which was kept cool. The solution was now carefully heated, when the aloisole made its way out of the pipette, and was thus exposed quite gradually to the action of the chromic acid. For half an hour, during which time the reaction lasted, aqueous vapour and carbonic acid were constantly given off, and at the same time the odour of bitter almonds was perceptible. The water collected in the recipient was milky, not acid, and possessed a powerful odour. On the supposition that oil of bitter almonds was formed in the reaction, the author repeated the experiment with 10 grms. of aloisole, and obtained a

milky liquid, which was immediately rendered clear by the addition of some æther. The æthereal solution left, on exposure to the air, some drops of oil, which were converted into benzoic acid in the course of two or three days. When oxide of copper is used instead of chromic acid, the same products are obtained; only a stronger heat is required, and a larger quantity of the oxide must be employed. This shows that aloisole, under the action of chromic acid or oxide of copper, is decomposed into water, carbonic acid and oil of bitter almonds, $C^{16} H^{12} O^6 + O^6 = C^{14} H^6 O^2 + C^2 O^4 + H^6 O^6$. With dilute nitric acid it likewise yields oil of bitter almonds; but as the products of distillation must naturally be acid, it is probable that it is immediately converted into prussic acid. Concentrated nitric acid acts so powerfully upon aloisole, that a kind of explosion sometimes takes place, a thick tarry kind of oil is formed, which consists almost entirely of aloïsic acid, and which is soon converted into picric acid, and a beautiful orange-coloured resin of the odour of oil of bitter almonds and oxalic acid. Chlorine water converts aloisole into aloïsic acid without any other substances appearing to be formed; during the operation the odour of bitter almonds is given off. On analysis aloisole yielded—

Carbon	61·54	60·28	60·42	8 =	600	61·54
Hydrogen .. 7·71	7·68	..	7·26	6	75	7·69
Oxygen	30·78	..	32·32	3	300	30·77

Aloïsic acid forms a thick brownish-red, somewhat turbid liquid, possessing a strong odour of castoreum, insoluble in water, but dissolving in every proportion in alcohol and æther. It boils in the anhydrous state at 482°, but is not volatile, so that it may be easily separated from any admixture of aloisole. When the acid is mixed with a very concentrated solution of potash or soda, they saturate it without losing their alkaline reaction, and it likewise expels no carbonic acid from carbonate salts. All the combinations of the acid are amorphous. The aloisate of barytes forms a white earthy, slightly acid powder, which may be obtained by double decomposition; on desiccation, even under the air-pump, all the salts are decomposed, and the acid may be extracted with æther. As, moreover, the aloïsic acid very soon becomes resinified by exposure to the air, the author found it impossible to obtain perfectly coincident results in the analyses.

The formula of aloisole does not agree with the general formula for the aldehydes, with which in other respects it has great similarity, for then it should consist of $C^8 H^8 O^3$ instead of $C^8 H^6 O^3$; however, the author thinks that notwithstanding this difference it must be arranged with that class of bodies.

If a strong current of chlorine be passed through a cold aqueous solution of aloes which has been evaporated to two-thirds of its volume, a yellow flocculent substance separates, upon which the liquid acquires a green colour, which only disappears after long-continued reaction. When the reaction has lasted from 24 to 36 hours, the precipitate, which had likewise become green, is destroyed, being converted into oxalic,

muriatic and carbonic acids. If the current of chlorine be discontinued as soon as the yellow precipitate has acquired a green colour and the liquid then poured off, there is perceptible on the sides and on the bottom of the vessel a resinous and laminar precipitate, which may be diffused in water to a paste. It is well washed with boiling water, which extracts muriatic acid and a considerable quantity of sulphate of lime and oxalic acid. The mass, exhausted with water, is then treated with cold, and subsequently with boiling alcohol, until this becomes of a bluish-red colour; it then remains upon the filter as a light flocculent precipitate, which consists for the greater part of sulphate of lime and coagulated vegetable albumen.(?) If the solution obtained with boiling alcohol is evaporated, a new body containing chlorine is obtained, which the author calls *chloraloile*. To purify this, it is washed with cold alcohol until the liquid which passes is perfectly colourless, when it is crystallized once or twice from boiling alcohol. It is not always possible to obtain this body even by carefully following the above process. Chloraloile crystallizes in light silky needles, is readily soluble in boiling alcohol and æther, and almost insoluble in cold alcohol. When the alcoholic solutions are very concentrated, they form a gelatinous mass on cooling. It melts at 284° to a transparent liquid, which solidifies on cooling to a crystalline mass; when heated in a retort to 311°, it boils and is entirely volatilized. It dissolves with a yellow colour in sulphuric, nitric and acetic acids, and is decomposed by them; when shaken with a solution of potash or soda and afterwards boiled, it is entirely decomposed, forming carbonated alkali and chloride. Ammonia absorbs considerable quantities of chloraloile, the liquid becoming yellow and subsequently red; upon the addition of acids, yellow flakes are separated which possess a totally different composition, and on evaporating the liquid at a gentle heat, only crystals of chloride of ammonium are obtained. Barytic water dissolves chloraloile readily with a purple colour, and the solution on evaporation gradually deposits crystals of chloride of barium. Conveyed into potash in a state of fusion, it does not yield any peculiar acid, but carbonate of potash and chloride of potassium. It consists of $C^{13}ClO^5$, and therefore contains no hydrogen like chloranile, to which in general it has a very great resemblance. However, the latter, $C^6Cl^2O^2$, is converted, by the action of caustic potash in a state of fusion, into chloranilic acid, while chloraloile is decomposed into carbonic acid and chlorine.

The brown resin which is extracted by cold alcohol in the preparation of chloraloile forms, when evaporated to dryness, an amorphous mass, which is insoluble in water, but dissolves in alcohol and æther, and behaves towards bases as a weak acid. Concentrated nitric acid converts it, under evolution of suffocating vapours, probably owing to the chlorine contained in the resin, into oxalic acid. The bluish body which remains on the filter after treating the precipitate produced by the action of chlorine upon solution of aloes, is sometimes as dark as prussian blue, and appears to consist of vegetable albumen coloured blue by the acid. It could not be more accu-

rately examined, but it evolved ammonia when heated, could not be decolorized with potash, and afforded a blue liquid with alcohol.

As soon as the first bubbles of a current of chlorine have passed through an alcoholic solution of aloes, it becomes much darker than previously, then brightens, assumes a pale orange colour, and finally separates into two layers, of which the upper one is alcohol, chloral, hydrochloric acid, acetic æther, &c. The lowermost one is semifluid, and consists for the greater part of an orange-coloured resin, which retains with great tenacity a tolerable quantity of chloral. If the resin be separated from the fluid, in order to dissolve it in alcohol of 0·86, and again exposed to a current of chlorine, it is entirely destroyed in the course of a few days; and in the fluid we find nothing further than the products of decomposition of alcohol by chlorine. When, on the contrary, the action of the chlorine is discontinued as soon as the alcoholic solution has passed from an orange to a pale yellow colour, a perfectly crystalline product is obtained, which the author calls *chloralise*. As it is, however, decomposed by muriatic acid, it must be removed as quickly as possible from the acid solution. For this purpose, the alcoholic pale orange-yellow liquid is emptied into a wide evaporating dish, which is heated in the water-bath to between 140° and 176°. To the liquid remaining after 2 hours' evaporation, twice its volume of cold water is added, when an abundant yellow precipitate appears, which consists almost solely of chloralise impregnated with chloral and with orange-coloured resin. The liquid is now poured off, and may be employed for precipitating fresh portions; the impure chloralise is collected on a filter, in order to remove from it the greater portion of the liquid with which it is impregnated, then dissolved in cold water, and the solution boiled. In this operation muriatic acid is driven off, while the orange-coloured resin is precipitated in brown flakes. The liquid, which had been previously filtered through moistened paper, deposits on cooling a yellowish powder, which examined under the microscope consists of radiately-grouped acicular crystals. By drying and washing with small quantities of cold æther, any still adherent chloral can be removed. The alcoholic residue is then dissolved in alcohol and the solution left to spontaneous evaporation, when small, silky, sulphur-coloured needles, which are completely devoid of odour, subside.

Chloralise is very sparingly soluble in cold water as well as in æther, but dissolves in every proportion in alcohol and boiling water. It melts at 158° without being decomposed, and yields no water if it had been well dried; at 356° it swells considerably, and acquires a reddish-brown colour; at 392° it is entirely decomposed, yielding a brownish oil, together with water and muriatic vapours. Potash, soda and ammonia dissolve chloralise with a yellowish-brown colour; if the alkali be saturated with an excess of acid, yellowish-brown flakes are precipitated, which have no longer any resemblance as regards composition to chloralise. If the latter be boiled with solution of potash or soda, a mixture of alkaline carbonate and muriate is obtained, as with chloraloile. Nitric, muriatic and sulphuric acids

readily dissolve chloralise; if water be immediately added to the solution, it is separated unaltered; but if left for any length of time, it is entirely decomposed. It differs from chloraloile by its composition, its non-volatility and its solubility in water and alcohol. The formula of chloralise is, according to the author, $C^{10} H^4 ClO$; its origin may be explained by the action of chlorine upon aloetine and alcohol in the following manner:—

$$C^6 H^{11} O^{10} + C^4 H^6 O^2 + Cl^6 = C^{10} H^4 ClO + H^{11} O^{11} + Cl^5 H^5.$$

The orange-coloured resin, which is formed at the same time with the chloralise, is insoluble in water, but readily soluble in alcohol, æther and the alkalies. When heated with nitric acid, it becomes of a beautiful red, subsequently dissolves, becomes colourless, and is completely decomposed into carbonic and formic acids. If the nitric solution be evaporated to dryness, a residue is obtained of sulphate of lime; and in one case the author moreover found some suberic acid.—*Journ. de Pharm. et de Chim.*, x. pp. 167, 241.

On the Alteration of Cellulose by Sulphuric Acid, and on the Solubility of Iodide of Starch. By H. Schacht.

In order to observe the blue colour imparted to cellulose by iodine after the action of sulphuric acid, an extremely thin section of a plant is placed on the object-bearer of a microscope, and moistened with a solution of iodide of potassium containing free iodine; the liquid which has not been absorbed is then removed with a hair pencil, and 1 or 2 drops of sulphuric acid (consisting of 4 parts rectified sulphuric acid and 1 part water) is conveyed by means of a glass rod to the object, which is immediately placed under the microscope. The cell-walls, which are coloured brown by the mere action of the iodine, appear blue after the addition of the sulphuric acid, while the contents of the cell remain brown.

Mulder attempted to prepare starch from cotton by means of sulphuric acid, but after removing the acid he always obtained a body which was no longer coloured blue by tincture of iodine. Mulder explains this by supposing that the half equivalent of water, which the cellulose has to part with in order to be converted into starch, again combines with the former on the addition of more water.

The author obtained, on repeating these experiments, a body which was certainly not coloured blue by tincture of iodine, but was so by iodide of potassium containing free iodine. To obtain this substance, 20 grms. of cotton were triturated in a porcelain mortar with 6 drms. of sulphuric acid of the stated strength. In the course of a minute the author obtained an almost colourless thick paste, which after 15 minutes resembled a thick syrup. Upon the addition of alcohol or water, a flocculent gelatinous mass was separated, which was coloured dark blue by treatment with solution of iodine. The acid mixture, precipitated with absolute alcohol and washed, or saturated with caustic soda and washed, left a substance which was coloured blue by solution of iodine, even when the acid had been

simply removed by means of water. The filtered liquid contained merely a trace of dextrine and no sugar; the washed precipitate was insoluble in boiling water, and did not swell; the liquid was coloured yellow by iodine. Under the microscope the precipitate exhibited a granular gelatinous appearance; nitric and muriatic acids produced no alteration; concentrated sulphuric acid dissolved the mass, as did also a solution of caustic soda. On drying, a yellowish horny mass was obtained, which swelled in water, and was coloured violet-blue by solution of iodine.

The substance thus obtained is at all events very closely allied to starch; and as a perfectly similar substance may be obtained from starch, it may be admitted that the formation of true starch in the metamorphosis of cellulose has been exceeded. A shorter duration of the action of the sulphuric acid always afforded the same substance mixed with undecomposed cotton; when the action was continued for a longer period, for example for about four hours, a substance was obtained which resembled Schleiden's amyloid in its properties. After eight hours' action scarcely any flakes of the amyloid were separated on the addition of water; the filtered liquid contained much dextrine and only a small amount of sugar. In the action of concentrated sulphuric acid upon cotton, the mass was rendered somewhat brown and liquid even in the course of half a minute, but was only rendered slightly turbid by water, and was not coloured blue by solution of iodine. The presence of inuline among the products of decomposition of cellulose could not be detected.

In the action of sulphuric acid upon arrowroot a thick mucus was obtained, which became thinner on trituration, and after 25 minutes deposited a substance, upon the addition of water, which was coloured blue by solution of iodine, and indeed behaved in every way similarly to the amylaceous body obtained from cotton. After 8 hours' action of the acid upon starch, the products were the same as with cotton; the starch, however, afforded somewhat more sugar; the cotton, on the contrary, more dextrine and little sugar.

The blue colouring of the starch by iodine cannot depend solely upon fine division, but is produced by a chemical combination; an assumption we are the more justified in making, as the iodide of starch is insoluble in acids. If ordinary starch is mixed with a little concentrated mineral acid or a solution of caustic soda, it is seen under the microscope very soon to dissolve, with the exception of the membranes. If, on the contrary, dry iodide of starch is placed along with sulphuric acid under the microscope, it continues, even after 24 hours, unaltered; it behaves in the same manner towards concentrated nitric acid. With pure muriatic acid of 1·195 spec. grav., the granules, which at first were dark, became lighter, and swelled to nearly 6 times their volume; and finally became coated, on becoming colourless, with crystals of iodic acid, which could be proved by acetate of morphine. Solution of caustic soda abstracts the iodine from the iodide of starch, and then destroys it. When

arrowroot is heated with water and an excess of iodine, the iodide of starch does not dissolve even after boiling for several hours; only when the iodine has evaporated does it swell and experience the known changes.

Wackenroder observes, with respect to the above statements, that the amylaceous body obtained by Schacht behaves exactly like that kind of starch which is often obtained in analysing plants; this is only rendered faintly blue by iodine, and sometimes not until concentrated nitric or sulphuric acid has been added. This may be explained from the iodine, instead of combining with the starch, acting upon other organic bodies, especially upon tannic acid, and it is only set free again by the addition of a strong acid. If some decoction of gall-nuts be added to iodide of starch, the colour disappears entirely, but is again rendered perceptible by the addition of nitric acid; but if the acid contain nitrous acid, the liquid still continues turbid, because either the iodine is oxidized or the starch destroyed.

To liberate the iodine from the iodides or from hydriodic acid, nitric and even hyponitric acid are best suited, according to Wackenroder, if not used in too large quantities. When the so-called white iodide of starch is moistened with concentrated nitric acid, it is coloured of a tolerably dark blue; but if a yellow or bluish hyponitric acid be used, scarcely a violet colouring results. Perchloride of iron effects the reduction of the iodine slowly, but with certainty, as an excess does not produce any injurious effect. Chlorine and bromine produce the yellow colour, but in the same manner they readily destroy it again; concentrated sulphuric acid likewise easily reduces the iodine from the iodides and hydriodic acid; sulphurous acid readily reduces the iodine from iodic acid, but as easily converts it into hydriodic acid. The blue colour of the iodide of starch, which has been destroyed by sulphurous acid, is again restored by a suitable addition of nitric acid. In general, of the above-named reagents, sulphuric acid deserves the preference in testing with iodine for starch, and nitric acid in testing with starch for iodine.—*Archiv der Pharm.*, xlvii. p. 157.

On the Acid Reaction of the Gastric Juice.

By Prof. C. G. Lehmann.

Pelouze, and especially Bernard and Barreswil, have shown with certainty the absence of free muriatic acid in the gastric juice. The author has obtained the same result, and at the same time he has indisputably proved the presence of free lactic acid. To obtain the gastric juice of dogs in the greatest state of purity possible, these animals were kept without food for from 12 to 16 hours, and then fed from 10 to 25 minutes before death with bones freed as perfectly as possible from skin and fat. Immediately after they were killed, the stomach was tied at the cardia and pylorus, and removed from the body. It was then opened by an oblique incision near the pylorus, and the fluid poured out, without the stomach being at the

same time much moved. The gastric juice thus obtained was almost perfectly clear, scarcely opalescent. The stomach of a dog of the size of a poodle contained from 15 to 40 grms. of a liquid, which flowed out spontaneously; that of a large pointer, from 30 to 90 grms. The fresh gastric juice was poured into a shallow broad flask, the mouth of which was closed by a cork, and through this a glass tube, bent four times at a right angle, was passed; the latter was covered with nitrate of silver on its inner side. The apparatus was placed under the air-pump with dry hydrate of potash, and exhaustion then applied. When the gastric juice had been evaporated until it was of a syrupy consistence, vapours of muriatic acid were evolved somewhat suddenly, so that the chloride of silver formed could be determined qualitatively and quantitatively. Treated in this manner, a gastric juice which was but slightly opalescent for instance, yielded 1·808 per cent. of solid residue, 0·125 per cent. muriatic acid, and 98·067 per cent. of water. This muriatic acid is formed by the decomposing action of the lactic acid at a certain degree of concentration, even in the cold, upon many chlorides, especially those of calcium and magnesium, but not the chlorides of potassium and sodium. To prove the presence of the lactic acid itself with certainty, the gastric juice was concentrated *in vacuo* to one-twelfth its volume, the residue mixed with alcohol of 0·85 spec. grav., the spirituous solutions from several stomachs evaporated to the consistence of a syrup, and the residue exhausted with absolute alcohol. The residue of this was exhausted with æther, and the æthereal extract mixed with water to remove the fat, and filtered. On further concentration, more drops of oil separated from the filtrate; moreover, the fluid about to be tested still contained muriate of ammonia. The liquid was partly saturated with lime, partly with magnesia, and the salts formed were purified by several recrystallizations from alcohol and water. The magnesian salt, dried at 266° F., and then incinerated, gave 16·666 per cent. of magnesia, 61·906 per cent. lactic acid, and 21·428 per cent. water; the formula $MgO, \overline{La} + 3HO$ requires 16·085 per cent. magnesia, 62·936 per cent. lactic acid, and 20·979 per cent. water. In some other experiments, fasting dogs were fed from 20 to 45 minutes before death with horse-flesh containing but little fat. The fluid which flowed spontaneously from the stomach, when filtered, left 5·602 per cent. of residue, and thus contained nutritive matters already in solution, which were detected by the copious precipitate produced by alcohol, or the formation of yellowish-brown films on evaporation. The gastric fluid thus obtained yielded no muriatic acid under the air-pump. From this fluid a magnesian salt was also obtained. I. gave 16·666 per cent. of magnesia, 62·122 $\overline{La}$, and 21·212 HO; II., which was obtained by exhausting the contents of the stomach with water, gave 15·966 per cent. MgO, 62·026 $\overline{La}$, and 21·008 per cent. of HO.—*Bericht der Gesellschaft der Wissenschaften in Leipzig*, p. 100–105.

On the Behaviour of the Metallic Cyanides when exposed to a high Temperature. By Prof. RAMMELSBERG.

Hitherto the process of decomposition which the metallic cyanides experience when heated in a closed vessel has been considered to be very simple; Gay-Lussac, however, already observed in the decomposition of the cyanide of mercury, that a small quantity of a brownish-black substance (Johnston's paracyanogen) was formed. Liebig and Redtenbacher also found that the cyanide of silver was converted by heat into sesquicyanide of silver with evolution of cyanogen, and that this was finally decomposed at a higher temperature into nitrogen and carburet of silver. According to Thaulow, however, there remains on heating the cyanide of silver a gray residue, which he calls paracyanide of silver, while he views the liberated gas as an isomeric modification of cyanogen (carbazote). According to the author, who was induced by these facts to make a series of experiments upon the decomposition of the cyanides, the cyanide of silver yields when heated the half of its cyanogen, and leaves Thaulow's paracyanide of silver. His carbazote is nothing further than cyanogen.

Prussian blue prepared from perchloride of iron and ferrocyanide of potassium does not lose the whole of its water until 482°, before which it is partially decomposed. Dried *in vacuo* over sulphuric acid, it contains 9 equivs. water, consequently just so much as to allow of its being regarded as the prussiate of the proto- and peroxide of iron. Heated in a retort over a lamp, it yields a black residue containing 14 per cent. carbon and as much nitrogen. The author considers this body to be a mixture of paracyanide of iron and carburet of iron. The ferrocyanide of hydrogen is decomposed at first into prussic acid and protocyanide of iron, which latter then likewise yields paracyanogen and carburet of iron. Ferrocyanide of potassium requires a very high temperature to be decomposed, and yields, after exhaustion of the cyanide of potassium, pure carburet of iron, FeC^2. Ferrocyanide of calcium is decomposed, even over a spirit-lamp, into cyanide of calcium and carburet of iron, pure nitrogen being evolved. Ferrocyanide of zinc yields paracyanide of zinc and carburet of iron. Ferrocyanide of lead disengages cyanogen and nitrogen, and leaves a mixture of paracyanides and carburets behind. Ferrocyanide of copper likewise parts with cyanogen and nitrogen. The residue consists of a mixture of paracyanides of copper and iron mixed with carbon. Cyanide of zinc is only altered at a strong red heat, when a portion is volatilized, and the black residue has the composition of the salt, but acids do not disengage prussic acid from it. Cyanide of nickel and cyanide of cobalt are decomposed with incandescence, when five-sixths of the nitrogen are liberated; the black residue must be regarded as paracyanide and carburet. Protocyanide of copper may be melted without decomposition; at a higher temperature a portion is converted into paracyanide, while the remainder is left unaltered.

The author observes that there is a cuprocyanide of potassium,

consisting of 2 atoms cyanide of potassium and 3 atoms protocyanide of copper, so that we are now acquainted with three such combinations. The smalt blue compound discovered by Döbereiner, which is formed when the protocyanide of platinum and potassium is precipitated with protonitrate of mercury, consists of 1 equiv. of the latter and 5 equivs. of the protocyanide of platinum and mercury, into which two constituents it is decomposed by heat.—*Archiv der Pharm.*, xlviii. p. 151.

On Guanine and its Compounds. By B. Unger.

Some time ago Unger asserted that xanthine, which he had discovered in guano, and uric oxide were identical*; these bodies, however, differ, as observed by Einbrodt, the uric oxide being insoluble both in muriatic and in oxalic acid. Moreover, Unger has since found that the so-called xanthine differs in composition from uric oxide, which is represented by the formula $C^{10} H^4 N^4 O^4$, and proposes on that account the name *guanine* for the substance occurring in guano. In its pure state it is colourless and free from sulphur.

Combination with Platinum.—In preparing this double salt, it is necessary to proceed in the following manner:—An excess of hot concentrated solution of platinum is poured into a hot saturated solution of guanine in muriatic acid, and boiled down to one-half its volume. In this operation no evolution of gas occurs, if the solution of chloride of platinum contain none of the oxides of nitrogen; and on cooling orange-yellow crystals are obtained, which are washed with alcohol or water, and dried over sulphuric acid; on burning they yield 35 per cent. platinum; they are not much more soluble in water than the ammonio-chloride of platinum; their powder is of a lemon colour. It is requisite in preparing them to keep the mixture boiling for some time, otherwise crystals of muriate of guanine separate at the same time as the double salt, and cannot be separated mechanically from one another. The formula of this compound is

$$C^{10} N^5 H^5 O^2 ClH, 2PtCl^2 + 4HO,$$

guanine being represented by $C^{10} N^5 H^5 O^2$.

Nitrates.—When a mixture of equal parts water and nitric acid of 1·25 spec. grav. is used for preparing the nitrate of guanine, long, extremely slender crystals in concentric groups are formed, which appear on rapid cooling to be matted together. Their solubility is enormously increased by heat, and they bear a boiling temperature without being decomposed. The same salt appears to form in every very dilute solution; its taste is at first acid, then astringent, and it strongly reddens litmus-paper; if, on the contrary, guanine is dissolved in nitric acid of 1·25 at 140°–176°, a salt crystallizes on cooling which contains the highest amount of acid hitherto observed, viz. twice that of the previous compound. The crystals consist of solid short prisms, and cannot be confounded with the preceding, from their remarkable external appearance. By mixing unequal proportions of the hot solutions of the two salts, the author lastly obtained two other combinations in definite proportions, which in appearance

* Chem. Gaz., vol. iii. p. 296.

as well as in composition may be regarded as the connecting links. All the salts effloresce in the air and lose some of their acid; they would probably lose the whole of it at a higher temperature, if this did not exert a decomposing action upon them. On analysis the salts gave the following formulæ:—

No. 1. $3C^{10}N^5H^5O^2 3NO^5 + 12HO$.
No. 3. $3C^{10}N^5H^5O^2 4NO^5 + 12HO$.
No. 4. $3C^{10}N^5H^5O^2 5NO^5 + 16HO$.
No. 2. $3C^{10}N^5H^5O^2 6NO^5 + 18HO$.

The neutral salt, which is formed on treating the base with muriatic acid, is $3(C^{10}N^5H^5O^5ClH) + 7HO$, and contains 10 per cent. water, which escapes below 212°; at 329° the whole of the muriatic acid is expelled and pure guanine left. The acid salt

$$C^{10}H^5N^5O^2, 2ClH$$

is formed by the action of dry muriatic acid gas at a moderate temperature upon guanine; the remainder is volatilized at 392°. The neutral sulphate of guanine is $C^{10}H^5N^5O^2, SO^3, HO + 2HO$; it loses at 248° 8·1 per cent. = 2 equivs. water; in contact with water it is decomposed into free acid and amorphous hydrate of guanine, $3C^{10}H^5N^5O^2 + 4HO$, which at 257° loses 7·1 per cent. water. The combination of guanine with soda, $C^{10}H^5N^5O^2, 2NaO + 6HO$, loses at 212° 33·3 per cent. = 6 equivs. water.—Liebig's *Annalen*, lix. p. 58.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Carburets of Iron. By M. Karsten.

The determinations of the amount of carbon in the different kinds of bar iron, steel and pig iron, are still variable and uncertain, partly owing to the estimation of the amount of carbon being very tedious if not difficult, and partly because the limits between bar iron and steel, as well as between steel and pig iron, are wholly undetermined, and are merely assumed conventionally from certain physical properties of the product. Combinations in definite proportions between iron and carbon are not to be met with in the carburets of iron; but the union of these two bodies continues uninterruptedly in indefinite proportions from 0 to the maximum amount of carbon, which is about 5·93 per cent. The classification of the carburets of iron in three divisions, bar iron, steel, and pig iron, is consequently not necessary, *i. e.* not required by the combining proportions, but wholly arbitrary.

To determine the amount of carbon, the best methods of separating the carbon from iron were employed; but in order to ascertain the degree of trustworthiness belonging to each, white pig iron, with a bright metallic surface, smelted with charcoal from sparry iron ore at the Sayner works near Bendorf on the Rhine, was submitted to

experiment. This pig iron contains no uncombined carbon (graphite), or at least mere traces; and the amount of combined carbon approaches closely to the maximum amount which iron is capable of taking up.

The amount of carbon of this pig iron was found, by different methods of analysis, as follows:—

	per cent.
By elementary analysis with oxide of copper, the carbon being calculated from the carbonic acid gas	4·2835
By elementary analysis with chlorate of potash and chromate of lead	5·7046
2nd experiment	5·6987
By decomposition of chloride of copper.....	5·5523
2nd experiment	5·6978
By decomposition of perchloride of iron:—	
1. Experiment with sublimed chloride of iron	5·4232
2. With perchloride prepared in the moist way	5·2867
By decomposition of chloride of silver	5·6056
2nd experiment	5·7234

As all bar iron contains more or less carbon, some decision should be come to as to the limits up to which it should be called bar iron, and below which steel. If the limits are fixed by calling that bar iron steel which becomes so hard by cooling in water after having been hardened that it gives sparks with quartz, this effect occurs only when the iron has taken up 0·5 of carbon. Iron which is perfectly free from foreign ingredients may even combine with 0·65 per cent. of carbon before attaining the above degree of hardness. The purer the iron and the less foreign substances (silicium, sulphur, phosphorus) it contains, the greater amount of carbon will it require in order to become much harder after the process of hardening than previous to it.

Iron which contains 0·5 to 0·65 per cent. of carbon is a very soft steel; the hardness and tenacity of the steel increase with the amount of the carbon. From 1·4 to 1·5 per cent. appears to be the limit at which steel exhibits after hardening the greatest hardness with the greatest tenacity; with more carbon the hardness increases, but the malleability and tenacity of the steel are diminished; when it amounts to 1·75 per cent. the steel is very slightly malleable; with 1·9 it can scarcely be welded red-hot, and with 2 per cent it breaks to pieces under the hammer. In this state the steel might already be called pig iron; but it may be beaten in the cold, and does not possess the property of separating a portion of its carbon in the form of graphite when allowed to cool very slowly after fusion. This occurs only when the carbon amounts from 2·25 or 2·3 per cent. If, therefore, a line of demarcation were to be drawn between steel and pig iron, which should be founded upon the combining proportions, 2·3 would characterize this limit.

The more carbon the pig iron takes up from that minimum to the maximum of 5·93 per cent., the lighter does the colour become, and the greater the hardness of the white variety, which is analogous to

hardened steel. The gray variety, with an equal amount of carbon, which is analogous to unhardened steel, will be softer, that is will separate the more graphite on solidification the slower the cooling. The gray pig iron, which contains the same amount of carbon as the corresponding white kind, may consequently be sometimes a mixture of white pig iron with graphite, sometimes of soft steel or of hard bar iron and graphite, according as the solidification resulted more or less slowly, and the solidified mixture retained more or less carbon in the combined state. When the solidification is sudden, gray iron is scarcely formed, because the entire amount of carbon remains chemically combined with the iron, and is not separated as graphite.

In preparing cast steel, the process is purely empirical, the eye of the workman being the weight and balance in determining the amount of carbon in the material to be employed. To manufacture cast steel with certain properties, such materials must be selected in which the amount of carbon is known, and which, by being fused together in accurately calculated proportions, produce a cast steel containing that amount of carbon which corresponds with the properties required of the cast steel to be prepared.—*Berichte der Berlin. Academie,* Nov. 5, 1846.

Preparation of Aurocyanide of Potassium for Electro-Gilding. *By* Alex. Kemp*.

Dissolve 1 part of gold in nitrohydrochloric acid, and render the solution as neutral as possible by evaporation to dryness; redissolve the chloride of gold in 8 parts of water, and heat the solution until it boils; add as much calcined magnesia as is equal to half the weight of the gold, and boil the whole till the liquid loses its yellow colour; the precipitate which forms is oxide of gold, with the excess of magnesia. Throw it on a filter, and wash it with boiling water until the liquid passes through tasteless. Having dissolved 8 parts of Liebig's cyanide of potassium in 80 of boiling water, pour it on the filter while still hot, it will dissolve the oxide of gold, leaving the magnesia unchanged. The same method may be followed in forming the silver solution, substituting nitric acid for the mixture of nitric and hydrochloric acids used in forming the gold solution.

College, Edinburgh, March 1, 1847.

PATENT.

Patent granted to James Napier, Shacklewell, Middlesex, for *Improvements in smelting Copper Ores.*

The object of this invention is to facilitate the operation of smelting copper ores, and this the patentee proposes to effect by the application of iron and alkaline substances, and by decomposing and disin-

* Communicated by the Author.

tegrating the products resulting from such application by means of water.

If the ores contain less than 20 per cent. of copper, and more than 2 parts by weight of sulphur to 4 parts by weight of copper, they are first subjected to the ordinary process of calcining and melting, to produce what is termed "coarse metal." If the ores contain less than 20 per cent. of copper and a smaller proportion of sulphur than that above mentioned, other ores, containing sulphur in a larger proportion, must be mixed therewith in such quantities that the average proportion of sulphur in the mixture will be 2 parts by weight to 4 parts of copper, and the mixture is then treated in the manner before mentioned for obtaining coarse metal. When the unmixed ores or the mixtures of ores contain more than 20 per cent. of copper, and a greater proportion of sulphur than 1 part by weight to 4 parts of copper, they are not subjected to the above processes of calcining and melting, but are treated at once in the manner described below for coarse metal.

To each ton of coarse metal, 56 lbs. of soda ash (containing about 50 per cent. of alkali) and 56 lbs. of slaked lime are added, and the mixture is put into what smelters term a "metal furnace;" when it is in a state of fusion, any slag that may have formed is skimmed off, and a quantity of scrap iron is introduced in the proportion of 1 cwt. thereof to each ton of coarse metal. As soon as this is melted, the whole is well stirred with a rabble; and the furnace being immediately tapped, the fused mass is run into sand-moulds. When the contents of the moulds are sufficiently set to be removed, they are put into a shallow pit, containing sufficient water to cover the whole, and allowed to remain therein from 2 to 3 hours, by which time the mass will have become partially decomposed and disintegrated. The excess of water is then run off, and the mass removed, and allowed to remain in a heap until the whole is reduced to a fine powder, which will be in about 24 hours. The powder is washed in any convenient manner, and introduced into a calcining furnace, in which the heat is gradually increased for 20 hours, so that at the expiration of this time a bright yellow heat will be obtained; and this yellow heat is continued for 6 hours longer, care being taken to prevent the heat from increasing to such a degree as would cake or fuse the powder, and to stir the powder regularly at intervals during the whole time. The powder is now withdrawn from the calcining furnace, and after being sprinkled with water, according to the ordinary practice, is introduced into a fusing or metal furnace; and for each ton of the powder about 1 cwt. of pulverized anthracite coal and 10 lbs. of sand are added; a further addition of a quantity of sand or fluor spar, as a flux, being made if found necessary. As soon as the whole is well fused, the slag is skimmed off, and the furnace tapped into sand-moulds. The product thus obtained is generally fit for the refining furnace; but if a small portion of it should be regulus, this regulus, which is rich in copper, is to be roasted, and afterwards refined. The slag above mentioned contains copper, and may be employed as a flux in charges for the ore-furnace as usual.—Sealed July 20, 1846.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Berberine and its Salts. By Th. Fleitmann.

In 1835 Buchner published an examination of berberine, which he had discovered, assigned to it the formula $C^{33}H^{18}NO^{12}$, and arranged it among the weak acids. The author has found, on the contrary, that it is a strong organic base. The berberine which he examined was also prepared by Buchner, according to whose observations it is precipitated by weak mineral acids from its solutions. The author attempted to turn this property to account, in order to purify the berberine; and, in fact, a moderately concentrated solution gradually solidified upon the addition of a few drops of muriatic acid to a tissue of silky yellow needles, which however could not be freed from acid either by recrystallization from water or alcohol. With sulphuric acid similar results were obtained; moreover, the berberine purchased of Buchner, and recrystallized several times, contained muriatic acid, and exhibited an acid reaction. It is therefore probable that Buchner examined berberine containing muriatic acid, for the author obtained, on analysing the muriate of berberine, exactly the same numbers as Buchner had formerly found, although the author previously proved the presence of 9 per cent. of chlorine in the compound. To obtain pure berberine, some sulphate of berberine was prepared by decomposing the muriate with weak sulphuric acid; the salt was then recrystallized, and dried at 212°, to expel all traces of muriatic acid. Barytic water was added to the solution of the sulphate until it became alkaline, when the liquid immediately assumed a dark red colour. To remove the excess of baryta, carbonic acid was passed through the liquid, which was then boiled and filtered, upon which the dark red solution was evaporated nearly to dryness in the water-bath, and dissolved in ordinary alcohol; the berberine was precipitated from this by æther, and recrystallized from water. The author found the decomposition of the sulphate of berberine by potash to be disadvantageous, and by ammonia imperfect.

Berberine, purified in the above-described manner, forms slender yellow needles. Dried over sulphuric acid, it still loses at 212° 19 per cent. water, and becomes reddish-brown. At 220° it melts to a resinous mass. When mixed with muriatic or sulphuric acid,

the solution becomes brighter, and after some time deposits, when not too dilute, crystals of the corresponding salt. On account of the colouring property, the reaction of the berberine could not be accurately determined; it appeared, however, to be neutral. It does not combine with the alkalies and alkaline earths. When heated with dilute caustic potash, the berberine separates and forms into lumps, which however contain no potash. The analysis of berberine, dried at 212°, gave—

	I.	II.			
Carbon	67·35	66·66	42	= 3150	67·35
Hydrogen	5·67	5·68	20	250	5·35
Nitrogen	..	..	1	177	3·78
Oxygen	..	..	11	1100	23·52
				4677	

Since the atomic weight of berberine in its combinations is 4452, and its formula consequently $C^{42}\,H^{18}\,N\,O^{9}$, that dried at 212° must contain 2 equivs. water. The berberine which had been dried under the air-pump lost 19·26 per cent. water; the formula,

$$C^{42}\,H^{18}\,NO^{9} + 2HO + 10HO,$$

requires 19·38 per cent.

Muriate of Berberine.—This was obtained by dissolving the commercial berberine, precipitating with muriatic acid, and recrystallizing until the acid reaction had disappeared. On account of the intense yellow colour of the solution, it is impossible to distinguish the reaction; but if the moist crystals of the compound are pressed between folds of bibulous paper, it absorbs the solution with which the crystals are drenched, but on further diffusion retains the dissolved salt, and then merely allows the solvent to pass, in which the presence of any free acid may be readily detected by test-paper. The muriate of berberine crystallizes, like all the other crystalline compounds, in slender yellow needles, and has in the air-dried state a yellow colour with a reddish tint. The substance, dried over sulphuric acid, lost, when heated in the water-bath, 8·65 per cent. water. The colour of the salt then changed to a yellowish-red. On exposure to the air, the salt dried at 212° rapidly reabsorbed water. The muriate of berberine for analysis was dried at 248°, and burnt with chromate of lead; the nitrogen was determined by Varrentrapp and Will's method. The analysis gave—

	I.	II.			
Carbon	62·81	62·49	42	= 3150	62·75
Hydrogen	5·44	5·67	20	250	4·98
Nitrogen	3·55	3·65	1	177	3·53
Oxygen	..	..	10	1000	19·90
Chlorine.....	9·01	8·78	1	442	8·85

The amount of hydrogen found is, according to the calculation, much too high, which appears to be owing to the hygroscopic nature of the substance. On adding concentrated nitric acid to the muriate of berberine, it was dissolved, forming a dark red liquid, which gave on supersaturation with ammonia a brown flocculent precipitate.

When this red solution was heated for some time, it acquired a brighter yellow colour, and was decomposed with evolution of nitrous vapours. When, in the presence of free nitric acid, it was evaporated to the consistence of a thick syrup, a peculiar yellow substance separated on the addition of water, which might be kneaded like wax in water, in which it was very sparingly soluble. Dissolved in alcohol, it yielded with solution of silver and solution of lead yellow precipitates. The formula which corresponds best with the amount of water eliminated from the crystallized muriate of berberine is

$$C^{42}\,H^{18}\,N\,O^{9} + HCl + 5HO,$$

which requires 8·23 per cent. water.

Bisulphate of Berberine is prepared by decomposing the muriate with dilute sulphuric acid. The reddish-yellow solution of the muriate of berberine assumed a bright yellow colour, and after some time deposited the bisulphate in minute reddish-yellow crystals, which, dried under the air-pump, experienced no loss in weight at 212°. The substance for analysis was dried at 212°, and burnt with chromate of lead:—

	I.	II.	III.				
Carbon.....	55·58	55·49	55·14	42	=	3150	55·46
Hydrogen.....	4·64	4·64	4·52	20		250	4·40
Nitrogen	..	..	..	1		177	3·13
Oxygen.....	..	..	..	11		1100	19·38
Sulphuric acid ..	17·90	18·08	..	2		1000	17·62

The bisulphate of berberine contains therefore 2 equivs. water of crystallization, and is represented by the formula

$$C^{42}\,H^{18}\,N\,O^{9} + 2SO^{3} + 2HO.$$

Bichromate of Berberine was prepared by adding bichromate of potash to a solution of muriate of berberine. The bichromate of berberine immediately separated as a very voluminous bright yellow mass, which was collected on a filter and carefully washed with water, in which it is very sparingly soluble. It dissolves very readily in strong acids. It loses no water at 212°. Dried and pulverized, it forms a bright yellow heavy powder, which on analysis yielded—

Carbon	54·52	54·65	42	= 3150·0	54·73
Hydrogen	4·48	4·12	18	237·5	3·91
Nitrogen.....	..	..	1	177·0	3·07
Oxygen	..	..	9	900·0	15·64
Chromic acid ..	22·39	22·15	2	1304·0	22·65

The bichromate of berberine yields, on dry distillation, abundant vapours of a yellow body of a peculiar odour, which condense to oily drops. The same body is obtained by heating pure berberine. When the bichromate is submitted to a gradually increasing heat, the entire mass is suddenly decomposed at a certain period, owing to the oxidizing action of the chromic acid; on further heating, only mere traces of yellow vapours are disengaged, and a cinder is left behind which it is very difficult to burn. The quantity of this yellow body was very small, and at least a pound of berberine must be operated

upon to obtain a sufficient quantity for accurate examination. It dissolved very readily in alcohol, and was thrown down by water as a yellowish-white precipitate. Neutral acetate of lead produced a yellow precipitate; nitrate of silver was reduced. The alcoholic solution exhibited a play of colours; the reflected rays of light were green, whilst the transmitted exhibited a red colour.

Nitrate of Berberine.—This salt was prepared by adding nitrate of silver to a solution of muriate of berberine. The liquid in which the chloride of silver and the precipitate of nitrate of berberine were suspended was heated, to dissolve the latter, and then filtered, and a few drops of dilute nitric acid added to the filtered solution, when the salt soon separated in very beautiful bright yellow crystals. It was recrystallized from water, to obtain it pure. Dried over sulphuric acid, it experienced no loss by heating in the water-bath. The salt was dried at 212°, and burnt with chromate of lead: it yielded—

Carbon	60·15	59·64	42 =	3150·0	60·11
Hydrogen	4·75	4·62	19	237·5	4·52
Nitrogen.....	..	..	2	354·0	6·75
Oxygen	..	..	15	1500·0	28·62

Consequently the formula is $C^{42}\,H^{18}\,N\,O^{9} + NO^{5} + HO$. The nitrate of berberine is remarkable by its pure bright yellow colour.

Chlorate of Berberine.—This was obtained from the muriate by decomposition with chlorate of potash. The yellow voluminous precipitate could only be partially freed by washing from chloride of potassium, as it is very soluble in pure water; while in a very dilute solution of chloride of potassium and chlorate of potash it is very sparingly soluble. It was therefore washed with water as long as the solution passed colourless through the filter, and the residuary chlorate of berberine recrystallized several times from alcohol, when it no longer left any residue on combustion. The crystals are of a yellow colour with a greenish tint, and like the nitrate contain no water of crystallization which passes off at 212°. It yielded on analysis—

Carbon.....	57·02	42 =	3150·0	57·25
Hydrogen	4·29	19	237·5	4·31
Nitrogen	..	1	177·0	3·21
Oxygen	..	15	1500·0	27·23
Chlorine	..	1	442·0	8·01

When struck, rubbed or ignited, the chlorate of berberine explodes, leaving a cinder which is not very easily burnt.

Combination of Berberine with Platinum.—This salt was prepared by adding chloride of platinum to a solution of the muriate of berberine. The nearly insoluble double chloride was very easily freed by washing with water from the excess of chloride of platinum. Dried under the air-pump, it experienced no loss at 212°. In external appearance it was scarcely to be distinguished from the chromate. On exposure to a moist atmosphere for some time, it becomes of a dirty colour, probably from incipient decomposition. It yielded on analysis—

Carbon	44·44	44·35	42 =	3150·0	44·83
Hydrogen	3·42	3·58	19	237·5	3·39
Nitrogen	..	..	1	177·0	2·52
Oxygen	..	..	9	900·0	12·77
Chlorine	..	..	3	1328·0	18·91
Platinum.....	18·11	..	1	1233·0	17·55

The formula for this combination is therefore

$$C^{42}H^{18}NO^{9} + HCl + PtCl^{2}.$$

Berberine exhibits a very peculiar and remarkable behaviour towards polysulphuret of ammonium; on adding to a solution of muriate of berberine sulphuret of ammonium saturated with sulphur, a brownish-red precipitate was instantly formed, which, collected on a filter and freed by washing from excess of sulphuret of ammonium, proved to be a sulphur compound, in which the sulphur no longer existed in the state of sulphuretted hydrogen, and could not be detected by the addition of a solution of lead. Nor was there any evolution of gas on even pouring concentrated muriatic acid upon this compound, nor any odour of sulphuretted hydrogen perceptible. A solution in water yielded with neutral acetate of lead a very beautiful red precipitate. The compound possessed a very disagreeable odour, somewhat resembling mercaptan, which likewise remained after treatment with an acid. Upon the addition of muriatic acid, the compound immediately assumed a lighter colour, and after a short time deposited yellowish-red crystals, which likewise afforded a red precipitate with a solution of lead. The compound appears to act the part of a base, and to enter into combination with acids. It melts somewhat above 212°, like pure berberine, apparently without being decomposed. A sulphur determination yielded 16·53 per cent. sulphur.—Liebig's *Annalen*, lix. p. 160.

On the Amount of Carbonate of Soda in the Blood.
By Prof. C. G. Lehmann.

If fresh blood which has been beaten be placed under the air-pump, and exhaustion be continued as long as a distinct evolution of gas occurs, and then a little acetic acid be added to the blood, on again exhausting, far more gas is evolved than before the addition of the acid; and even if covered by a layer of oil, it froths so strongly that whenever the vessel is filled with more than three-fourths it runs over. To determine the amount of carbonic acid contained in the blood in a state of combination, the gases contained in the fresh and beaten blood of oxen were withdrawn by hydrogen and long-continued exhaustion with the air-pump. The hydrogen gas, which was purified by solution of bichloride of mercury, distilled sulphuric acid and dry hydrate of potash, was transmitted for from half an hour to an hour through the blood placed in a flask holding about 2 to $2\frac{1}{2}$ lbs., and covered with a layer of oil. A smaller flask, the bottom of which was covered with oil, was connected to that containing the blood; and to this a bulb-apparatus, filled with solution

of acetate of lead and a little acetic acid, was added, to see whether the blood remained undecomposed throughout the entire duration of the experiment. Two bulb-apparatus, containing sulphuric acid, served to absorb the aqueous vapour, which was copiously evolved during the pumping; and lastly, the carbonic acid which escaped was estimated by dry hydrate of potash.

After the hydrogen had been passed through this apparatus for a considerable time, the latter was joined to a larger air-pump, and the cock between the vessel containing the blood and the apparatus for purifying the hydrogen was closed. On account of the great frothing, not more than about 5 strokes of the pump were made in half an hour; and this was continued for nearly 3 hours. After this, when the entire apparatus had gradually become again filled with hydrogen, the increase in weight of the potash-apparatus was determined. Acetic acid was now added to the vessel containing the blood, without the admission of atmospheric air, and the same proceeding adopted as before the addition of the acid. A series of 10 experiments gave,—

Weight of ox-blood in grms.	Before the addition of acetic acid.			Temperature.	After the addition of acetic acid.			1000 grms. of blood contain of	
	Duration of		CO_2 found.		Duration of		CO_2 found.	free CO_2.	combined CO_2.
	the evolution of H.	the pumping.			the evolution of H.	the pumping.			
	h m	h m			h m	h m			
768	1 30	2 50	0·091	72–79	1 30	2 40	0·545	0·118	0·7124
1051	1 5	3 00	0·133	77–84	0 45	2 55	0·623	0·126	0·5927
1025	0 35	2 55	0·135	73–86	1 00	4 00	0·729	0·131	0·7110
1120	1 50	3 00	0·147	82–95	0 45	3 5	0·770	0·131	0·6880
1147	1 20	2 50	0·198	72–77	0 50	3 15	0·788	0·172	0·6700
1152	0 15	3 00	0·124	73–77	0 45	3 00	0·752	0·107	0·6527
1062	1 00	4 00	0·213	79–86	0 30	3 45	0·617	0·204	0·5810
1168	1 00	3 5	0·120	82–88	0 45	3 10	0·786	0·102	0·6729
1091	0 15	3 15	0·105	86–91	0 45	2 45	0·835	0·096	0·7653
1026	0 20	3 00	0·136	86–93	0 30	3 10	0·732	0·132	0·7134
							Mean...	0·132	0·6759

Calculated by volume, 1000 cub. centim. of well-beaten and fresh ox-blood lose about 70 cub. centim. of carbonic acid by mechanical means, and 360 cub. centim. when acid is used. 100 grms. of blood thus contain 0·0676 grm. of combined carbonic acid; and if this is in combination with soda, 0·1628 grm. of neutral carbonate of soda. Since, according to the author, beaten ox-blood contains 21·5 per cent. of solids, which contain 3·58 per cent. of ash, and this 86·0 per cent. of soluble salts, 100 grms of the latter must contain 24·364 grms. of carbonate of soda.

To determine the quantity of carbonic acid in the salts of the blood directly, the blood was mixed with an equal volume of water, and the whole of the constituents of the blood, but not at one time, were coagulated by heat; the expressed liquid was then evaporated, and repeatedly filtered from the flakes which separated. The residue

was incinerated in a platinum crucible, at the lowest possible heat, until it was semifluid in the hottest part of the crucible. The mass, which still contained carbon, was digested with distilled water, and the carbon with the insoluble salts placed upon a weighed filter, which was subsequently burnt to determine the amount of insoluble salts. The soluble salts were analysed in the ordinary manner, the carbonates being determined by chloride of barium, &c. They yielded—

	I.	II.	III.
Sulphate of soda	4·100	3·630	4·382
Phosphate of soda ($3NaO, PO^5$)	3·722	3·688	3·708
Carbonate of soda	15·830	18·052	16·626
Alkaline chlorides	75·481	73·945	75·030

In one experiment with Fresenius's apparatus, 17·034 per cent. of carbonate of soda were found, which agrees very well with the above analyses; in a second, 18·771 of it were obtained. According to the determinations of the carbonic acid found in blood, 100 parts of the soluble salts of the blood contain 24 parts of carbonate of soda; whilst we find, from the previous data, that 100 parts of the soluble salts of the extractive matter of the serum contain 17 parts of it.—*Bericht über die Verhandlungen der Gesellschaft der Wissenschaften in Leipzic*, p. 96–100.

Observations on Gun-Cotton.
By MM. Schönbein *and* Böttger.

The authors have found that the best solvent for explosive cotton is acetic æther, by which means it may be obtained perfectly pure: the substance, thus purified and dried at 212°, yielded on analysis—

			Xyloidine according to Ballot.	
	Found.	Calculated.	Found.	Calculated.
Carbon	27·43	28·1	37·29	37·31
Hydrogen	3·54	3·1	4·99	4·84
Nitrogen	14·26	14·5	5·17	5·76
Oxygen	54·77	54·3	52·55	52·09

The composition of gun-cotton is consequently very different from that of xyloidine*; the latter is dissolved by warm concentrated acetic acid, and is again separated upon the addition of water, while gun-cotton is insoluble in it. Xyloidine dissolves moreover in muriatic acid of 1·12 spec. grav. when boiled for some length of time; likewise in nitric acid of 1·38 spec. grav. to a colourless liquid, from which no precipitate results on the addition of water; gun-cotton is not acted upon by these two acids. Xyloidine dissolves partially in absolute alcohol, and almost entirely in æther containing alcohol to a colourless gelatinous mass, which when spread upon a smooth surface leaves a dull white opake membrane; gun-cotton is almost insoluble in these liquids. Xyloidine mixed with charcoal burns

* This has long been shown by Pelouze and other chemists. See pp. 18 and 55 of the present volume.—Ed. *Chem. Gaz.*

quietly, leaving a carbonaceous powder; gun-cotton burns instantaneously without any residue. Xyloidine ignites at 356°; gun-cotton at 446°; and also between 347° and 392°, when it has been exposed to these temperatures for some minutes.—*Pharm. Cent. Blatt.*, Jan. 27, 1847.

Further Observations on the Potato Disease.
By George Kemp, M.D. Cantab.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—In a paper, which I recently forwarded to your Journal, on the potato disease, it was a matter of regret to me that circumstances prevented my appending a few notes in acknowledgment of the authorities to whom the research is much indebted.

The actual discovery of butyric acid in the diseased tuber is exclusively due to Mr. Tilley, who in the autumn of 1845 published the fact in the 'Times.' I unfortunately did not take notes of his paper, hoping to see a more complete *resumé* of his labours in the 'Chemical Gazette.' That he was perfectly correct in his statement I can aver, having repeatedly obtained the characteristic odour of the acid in question by simply adding sulphuric acid to the pulpy mass, the temperature being at the same time gently raised over the lamp.

Some time previously MM. Erdmann and Marchand made the important discovery, that butyric acid is formed during the fermentation of various kinds of seeds, moisture and atmospheric air being apparently necessary conditions. For an abstract of their researches the English reader is indebted to the Chemical Gazette, vol. i. p. 705.

At a subsequent period Prof. Scharling traced the same change as occurring during the fermentation of potatoes. (Chem. Gaz., vol. ii. p. 447.)

Berzelius (vol. vii. p. 384) has given us a connected view of the proximate analyses of Einhof, Pearson, Lampadius and Henry; to which Prof. Thomson, in the interesting portion of his Vegetable Chemistry included between pp. 838 and 842, has added a syllabic view of the excellent practical experiments of Mr. Skrimshire, with other matter of great importance.

In addition to the general conclusions which I have already ventured to advance, and in pursuance of a subject which has involved much labour and anxiety, I beg to conclude with a hypothesis, which has been forwarded to a few scientific friends, and which appears, in the present state of our knowledge, to account for most of the phænomena present.

It seems that, from the first formation of the potato tuber, two sets of forces are in operation, which may be designated forces of aggregation and forces of reproduction; and to the relative position in which these forces stand towards each other, the phænomena in question are referred; thus, during the growth of the tuber, the conditions present are such as favour and promote the action of

the former, diminishing however in proportion as the maximum growth is attained; at this point, under the influence of vitality, other conditions become developed favourable to the action of the latter forces, and in a degree so nearly equal to the former as to establish a state of repose. This, however, cannot be considered as an absolute state of statical equilibrium, the conditions now present being favourable to the operation of the forces of reproduction, the influence of which is, in the normal condition of the tuber, inappreciable. At length accumulating, and that at a period when the most favourable (vernal) influences are also present, these forces so far preponderate as to exhibit all the phænomena of germination.

In the diseased potato the case is different; up to a certain point the forces of aggregation operate as usual, but are suddenly counteracted by the latter, which proceed, with a morbid rapidity and intensity, to effect certain changes in molecular arrangement. During the year 1845 vitality was in most cases suddenly arrested, and then certain organic but unorganized bodies, which also make their appearance during the germination of seeds and tubers, were the result; in the year 1846, vitality not being immediately destroyed, sprouts and tubers were reproduced; this phænomenon occurring, however, in most cases, long before the original tuber had arrived at maturity.

If the above hypothesis be correct, the whole problem resolves itself into "*the determination of the conditions under which these forces mutually counteract each other, or by which their normal mode of action, either as to order or intensity, becomes disturbed.*"

I remain, Sir,

Your obedient Servant,

St. John's, Isle of Man,
March 18, 1847.

Geo. Kemp.

Observations on Cholesterine. *By* L. Schwendler *and* E. Meissner.

Cholesterine with Water of Crystallization.—Cholesterine crystallized from alcohol parts with 5 per cent. water when warmed, without any change of appearance. It seems however only to be hygroscopic water. On the other hand, a combination of cholesterine with a definite proportion of water is obtained when a saturated solution in æther is mixed with about half a volume of alcohol and left to spontaneous evaporation; cholesterine is then deposited in large, well-formed, but very thin tabular crystals. On exposure to the atmosphere they retain their transparency, but when heated become opake, milky, and of a nacreous lustre, losing water. In four experiments 100 parts of cholesterine lost, after it had been dried at 212° over chloride of calcium, on cautious heating to fusion, 2·87, 2·77, 2·79, 2·897 per cent. water. This amounts on an average to 2·83 per cent., or 2 atoms to 1 atom of cholesterine, according to which it should be 2·90. The difference is to be ascribed to the circumstance that the hydrated cholesterine begins to lose water over dry substances even at the ordinary temperature, as distinctly exhibited

at several places on the crystals by white spots. The hydrated cholesterine does not form rhombohedral prisms, but different kinds of oblique prisms, which have exactly the lustre and fracture of crystallized gypsum. Pure carefully-fused cholesterine constantly solidifies on cooling to a silky mass of fasciculate, arborescent and radiate groups of crystals.

Composition of Cholesterine.—An analysis made with perfectly pure fused cholesterine, with the employment of oxygen gas towards the conclusion of the combustion, gave the following result:—

Carbon	84·20	28	84·037
Hydrogen	12·00	24	11·967
Oxygen	3·80	1	3·996

It is, however, not probable that a body with such properties as cholesterine should possess so simple an atomic composition; moreover, the hydrated cholesterine would then have to be regarded as a combination of 3 atoms of cholesterine with 2 atoms of water. It is probable that the true atomic weight of cholesterine is three times as great, and must be expressed by the formula $C^{84}H^{72}O^{3}$. The hydrated cholesterine would then be $C^{84}H^{72}O^{3} + HO$. Cholesterine contains neither nitrogen, sulphur nor phosphorus.

Cholesterine and Chlorine.—Dried pulverized cholesterine, exposed to a current of dry chlorine, becomes so much heated that it melts and disengages muriatic acid gas, at the same time acquiring a yellow, and subsequently a brown colour. If the current of chlorine be moderated and the cholesterine kept cool, it merely cakes slightly together, remaining white; it is, however, very difficult to complete the action entirely in this manner, notwithstanding it is so violent at the commencement, and to obtain a product of constant composition. This was attained, however, by reducing the fused cholesterine again to a fine powder, and spreading it out in a thin layer upon the bottom of a very spacious flask, and passing a small quantity of dried chlorine gas into the air in the flask, which is kept cool externally. The flask was then closed, and kept, being frequently agitated, until the colour of the chlorine had disappeared, when a further quantity was passed into it. The chlorine which disappeared was always replaced by muriatic acid gas. This was continued for several days, and, the mass being reduced to powder, left in contact for a considerable time with undiluted chlorine, upon which this and the muriatic acid gas were expelled by dry air. The substance for the analysis was kept for a long time over hydrate of potash.

The product thus obtained is a white loose powder, void of taste and smell; it adheres between the warm fingers like a resin, melts at 140° to a yellowish liquid, and solidifies to an amorphous mass; a few degrees above this temperature it disengages a large quantity of muriatic acid, and is converted into a brown porous resinous mass; it is not moistened nor altered by water; cold alcohol of 0·868 does not dissolve it; when warmed with it, it gradually cakes together, and melts below the boiling-point to a liquid of the colour and con-

sistence of the yolk of egg; when heated for some length of time, the colour became still darker, and a mere trace was dissolved by the alcohol. It behaves similarly towards absolute alcohol. Cold æther dissolves it entirely, although with difficulty. On spontaneous evaporation it separates in white, transparent, perfectly amorphous granules. Warm æther dissolves it readily and entirely, but it does not crystallize from the solution nor from a mixture of alcohol and æther. It is rendered more or less yellow or brown by the slightest heat. It is not altered by a solution of hydrate of potash or ammoniacal gas; but when warmed with it, becomes brown and resinous. When kept for a long time in a closed vessel, some muriatic acid gas is evolved from it. The determination of chlorine was effected by ignition with caustic lime in a glass tube, &c.; the combustion with the assistance of a long layer of oxide of copper, and the employment of oxygen towards the conclusion. The analysis yielded—

Carbon	48·74	50·64	49·35	84	49·77
Hydrogen.....	6·05	5·90	5·94	60	5·90
Chlorine	41·03	41·71	40·90	12	41·95
Oxygen.....	4·18	1·75	3·81	3	2·38

Undoubtedly several definite intermediate compounds exist, as $C^{84}H^{69}Cl^{3}O$ and $C^{84}H^{63}Cl^{9}O^{3}$:

this was rendered evident by several analyses. Bromine acts in the same manner as chlorine on cholesterine; it is converted by the action of bromine gas diluted with air, with evolution of hydrobromic acid into a pale yellow, loose, pulverulent compound, which behaves exactly like the chlorine compound, and without doubt possesses a similar composition.—Liebig's *Annalen*, lix. p. 107.

ANALYTICAL CHEMISTRY.

On a new Method of analysing Nitrates, and especially Saltpetre. By J. Pelouze.

A method has recently been proposed by M. Gossart for appreciating the degree of purity of crude nitre, by mixing it with sulphuric acid, and decomposing it by a solution of sulphate of iron of known strength*; the operation is complete when, after having heated the mixture and removed a small quantity, ferridcyanide of potassium indicates in it the presence of protoxide of iron. This method is founded upon the principle which Gay-Lussac and several other chemists have applied to chlorimetry and the assaying of manganese ores, that is to say, it consists in appreciating the limit of certain phænomena of peroxidation or perchlorination in which the substance submitted to analysis intervenes. The idea is a very happy one, and justly belongs to M. Gossart; in repeating his pro-

* See page 99.

cess, however, I found it to be accompanied with certain imperfections; and have been led, from the following observations and experiments, to the process for the analysis of nitrates, which will be described in the following pages.

Of all the metals iron is one of those the salts of which are most readily peroxidized; it is known, from the experiments of M. Marguerite, that a dilute solution of protochloride of iron is instantly peroxidized when a solution of permanganate of potash is added to it at the ordinary temperature, and that the addition of the smallest quantity of mineral cameleon to a salt of iron thus peroxidized communicates to the liquid a rosy tint, which accurately indicates the completion of the peroxidation.

I first accurately determined how much pure nitrate of potash was requisite to peroxidize a known weight of iron dissolved in an excess of hydrochloric acid; I found that 2 grms. of pure iron (pianoforte wire), dissolved in a considerable excess of hydrochloric acid, required from 1·212 to 1·220; on an average, therefore, 1·216 grm. of pure nitrate of potash. I examined the nature of the gases given off in this reaction, and I found them to consist of hydrochloric acid and deutoxide of nitrogen. Converting these numbers into equivalents, they correspond to 6 equivs. of iron and 1 equiv. of nitrate of potash; the acid of this last salt, therefore, is decomposed into deutoxide of nitrogen, which is disengaged, and into 3 equivs. oxygen, which deprive the hydrochloric acid of 3 equivs. hydrogen, to form 3 equivs. water and liberate 3 equivs. chlorine, which produce with the 6 equivs. protochloride of iron 3 equivs. of perchloride, as indicated by the following equation:—

$$6FeCl + NO^5KO + 4HCl = 4HO + KCl + NO^2 + 3(FeCl^3)*.$$

This decomposition being well established, it was easy to conceive that it might become the basis of a ready and simple method of analysing the nitrates. It was not probable indeed that the presence of chlorides and sulphates in those salts, and especially in nitre, would in any way interfere with the mode of decomposition; and I found by experiment that, in whatever proportion present, those salts had no influence whatever upon the quantity of nitrate requisite to peroxidize the iron. This new point well established, it was evident that, to complete the new method, there only remained to be found a safe and ready method of determining, in the assay of an impure nitrate, the quantity of iron not peroxidized; and such a method, as the reader is aware, has been described by M. Marguerite.

I will suppose, for instance, that having operated upon 2 grms. of iron and 1·216 of impure nitre, the mineral cameleon indicates that 0·200 iron has not been peroxidized; I conclude that 2 grms., minus 0·200, or 1·8 grm., has been peroxidized; now if the salt had been pure, the 2 grms. of iron should have been entirely peroxidized. I have therefore the proportion

$$2{\cdot}000 : 1{\cdot}216 :: 1{\cdot}800 : x = 1{\cdot}0944;$$

* This decomposition of nitrates by protosalts of iron in the presence of an excess of hydrochloric acid furnishes an excellent method of preparing the deutoxide of nitrogen.

the 1·216 grm. of impure nitre consequently contained 1·0944 nitrate of potash, or 90 parts in 100 of the salt.

I will select, as an example of the new method of estimating the nitric acid and analysing the nitrates, the crude nitre of commerce as it is sent to the refiners. I place 2 grms. of harp wire in a flask capable of holding 150 cubic centimetres, and pour upon it from 80 to 100 grms. of strong hydrochloric acid; and after having closed the flask with a cork furnished with a drawn-out tube, the iron is dissolved at a gentle heat. When the whole is dissolved, 1·200 grm. of the nitre under examination is introduced; the flask is immediately closed, and the liquid boiled; it becomes of a brown colour; dense vapours of hydrochloric acid, mixed with deutoxide of nitrogen, issue from the orifice of the drawn-out tube, and prevent the access of air. As soon as the liquid loses the brown colour, it becomes yellow, and gradually brightens; after boiling for 5 or 6 minutes, and when the liquid has become perfectly transparent, the flask is removed from the fire, the liquid which it contains and the wash-water are poured into a flask capable of holding about 1 litre, which is then entirely filled with ordinary water; upon this a solution of permanganate of potash of known strength is gradually added from a graduated burette. The flask is agitated so as to mix the liquid; and as soon as this assumes a faint rosy tint the addition of permanganate is discontinued, and the quantity employed to peroxidize the iron read off on the burette. The operation is then finished, and we have only to calculate the result*.

We will now suppose that the solution of mineral cameleon was of such a strength that 25 cubic centimetres were required to peroxidize 0·500 of iron, or 50 cubic centimetres for 1 grm. of that metal; and we will also suppose that to complete the preceding experiment 10 cub. centim. of the same solution were required; now if 50 cub. centim. of this permanganate of potash suffice to peroxidize 1000 of iron, how much ought 10 cub. centim. to peroxidize?

$$50 \text{ c. c. } : 1{\cdot}000 :: 10 \text{ c. c. } : x = 0{\cdot}200.$$

I subtract therefore from the 2·000 of iron 0·200, and I conclude that the remaining 1·800 have been peroxidized by 1·200 crude nitre; but I know that 2·000 of iron represent 1·216 pure nitrate of potash, or that 1 grm. represents 0·608, and I find the quantity of that salt corresponding to 1·800 of iron by the following proportion:—

$$1{\cdot}000 : 0{\cdot}608 :: 1{\cdot}800 : x = 1{\cdot}0944.$$

In the 1·200 of salts submitted to analysis there was consequently 1·0944 pure nitrate of potash, or $\frac{1{\cdot}0944}{1{\cdot}2000} = 91{\cdot}2$ per cent.

It will readily be understood that, in the experiment just mentioned, in the reaction between the protochloride of iron and nitrate, access of air should be guarded against; otherwise this would rapidly act upon the deutoxide of nitrogen, and render it capable of peroxi-

* For the method of preparing the permanganate of potash see M. Marguerite's paper, Chemical Gazette, vol. iv. p. 219.

dizing a further quantity of iron, so that the amount of the nitre would be exaggerated. This inconvenience however is readily avoided; as soon as the iron has disappeared in the acid, the flask is filled with hydrogen and hydrochloric acid gas; the nitrate which is introduced carries with it but a mere trace of air, if any; and the liquid kept boiling disengages by the drawn-out tube acid and aqueous vapours, the issuing forth of which being always visible and readily maintained, does not allow the admission of any air. Moreover, the presence of air is only to be feared when the nitrate has just begun to act; for I have convinced myself of the accuracy of the assertion of M. Marguerite, that iron is peroxidized in a strongly acid liquid, even on exposure to the air, with great difficulty, and so slowly that the analysis is not sensibly affected by it.

The nitrates may be employed either in the solid state or in solution in water. I generally prefer them in the former condition; but in the case of crude nitre, as very considerable differences may exist in the samples, the mean composition of which is to be determined, it will perhaps be preferable to operate upon a solution made with a large quantity of substance. In such a case I dissolve 120 grms. of the nitre to be examined in a vessel capable of holding 2 quarts, or 60 grms., in a flask holding 1 quart, which is finally filled exactly with ordinary water. I take with a pipette 20 cubic centimetres of this liquid, which I pour into the solution of 2 grms. of iron in 100 grms. of concentrated hydrochloric acid just as the metal has disappeared, and proceed as before. It is evident that 20 cub. centim. of such a liquid contain 1·200 grm. of crude nitre; it is consequently precisely the same as if we were operating upon that quantity of dry salt.

I have submitted to the same test the pure nitrate of soda as well as the impure, such as it occurs in commerce, the nitrate of ammonia and the nitrate of lead; all the results confirmed the accuracy of the new method.

This method will enable us to determine the proportion of water contained in certain nitrates in many cases where this is still doubtful; it will prove of great value in analysing mixtures of nitric and sulphuric acid destined for the preparation of gun-cotton, as the sulphuric acid in no way interferes with the new mode of analysis; nitric acid, diluted with water only or mixed with sulphuric acid, may be estimated just as easily as a neutral nitrate. But it is principally in determining the value of crude saltpetre that the new method will prove of the greatest utility. In most cases the saltpetre of commerce contains only one nitrate, that of potash, which is mixed with earthy matters, sulphates and alkaline chlorides; such is the case with that imported from the East Indies. Its analysis may therefore be made with the greatest accuracy and quickness by the method which I propose. I must however observe that it does not indicate the nature of the base combined with the nitric acid, but only the quantity of nitric acid; so that in order to apply it to the analysis of a special nitrate, it will be requisite to ascertain that the substance submitted to analysis contains no other salt of the

same kind. For instance, I can easily appreciate the exact proportion of nitrate of potash mixed with sulphates and chlorides; but if any nitrate of soda exist in the mixture, my process merely indicates the quantity of nitric acid combined with an unknown proportion of these two bases. In this respect it resembles the mode of analysis described by Gay-Lussac, which consists in decomposing the alkaline nitrates by charcoal, and estimating with a standard solution of sulphuric acid the resulting proportion of carbonates. It is evident therefore that it cannot be exclusively substituted for the present method of ascertaining the value of nitre; but there can be no doubt that, when employed concurrently with the old method, it will be of great use to the manufacturers of gunpowder. At all events, the new method, when applied in the case of a nitrate the base of which is known, offers the advantage of being easily executed, requires scarcely 20 minutes, and is accurate to within from two to three-thousandths.—*Comptes Rendus*, Feb. 15, 1847.

On a new Test for Prussic Acid, and on a simple Method of preparing the Sulphocyanide of Ammonium. *By* Prof. Liebig.

When some sulphuret of ammonium and caustic ammonia are added to a concentrated aqueous solution of prussic acid, and the mixture heated with the addition of pure flowers of sulphur, the prussic acid is converted in a few minutes into sulphocyanide of ammonium. This metamorphosis depends on the circumstance, that the higher sulphurets of ammonium are instantly deprived by the cyanide of ammonium of the excess of sulphur they contain above the monosulphuret; for instance, if a mixture of prussic acid and ammonia be added to the pentasulphuret of ammonium, the solution of which is of a deep yellow colour, and the whole gently heated, the sulphuret of ammonium is soon decolorized; and when the clear colourless liquid is evaporated, and the admixture of sulphuret of ammonium expelled, a white saline mass is obtained, which dissolves entirely in alcohol. The solution yields, on cooling or evaporation, colourless crystals of pure sulphocyanide of ammonium. Only a small quantity of sulphuret of ammonium is requisite to convert, in the presence of an excess of sulphur, unlimited quantities of cyanide of ammonium into sulphocyanide; because the sulphuret of ammonium, when reduced to the state of monosulphuret, constantly reacquires its power of dissolving sulphur and transferring it to the cyanide of ammonium. The following proportions will be found to be advantageous:—2 oz. of solution of caustic ammonia of 0·95 spec. grav. are saturated with sulphuretted hydrogen gas; the hydrosulphate of ammonia thus obtained is mixed with 6 oz. of the same solution of ammonia, and to this mixture 2 oz. of flowers of sulphur are added; and then the product resulting from the distillation of 6 oz. prussiate of potash, 3 oz. of the hydrate of sulphuric acid, and 18 oz. water. This mixture is digested in the water-bath until the sulphur is seen to be no longer altered and the liquid has assumed a yellow colour; it is then heated to boiling, and

kept at this temperature until the sulphuret of ammonium has been expelled and the liquid has again become colourless. The deposited, or excess of, sulphur is now removed by filtration, and the liquid evaporated to crystallization. In this way from $3\frac{1}{3}$ to $3\frac{1}{2}$ oz. of dazzling white dry sulphocyanide of ammonium are obtained, which may be employed as a reagent, and for the same purposes as the sulphocyanide of potassium. Of the 2 oz. of sulphur added, $\frac{1}{2}$ an oz. is left undissolved.

The behaviour of the higher sulphurets of ammonium towards prussic acid furnishes an admirable test for this acid. A couple of drops of a prussic acid, which has been diluted with so much water that it no longer gives any certain reaction with salts of iron by the formation of prussian blue, when mixed with a drop of sulphuret of ammonium and heated upon a watch-glass until the mixture is become colourless, yields a liquid containing sulphocyanide of ammonium, which produces with persalts of iron a very deep blood-red colour, and with persalts of copper, in the presence of sulphurous acid, a perceptible white precipitate of the sulphocyanide of copper. —Liebig's *Annalen*, Jan. 1847.

Modification of Varrentrapp *and* Will's *Tube employed in the Determination of Nitrogen. By* Alex. Kemp*.

Any one who has followed Varrentrapp and Will's method of analysing nitrogenous organic bodies must have experienced the inconvenience and difficulty attending the use of the tube employed by them to condense the ammoniacal vapours, from the great tendency to regurgitation of the acid liquid, and the consequent destruction of the combustion-tube from a drop of the liquid coming into contact with it when at a red heat.

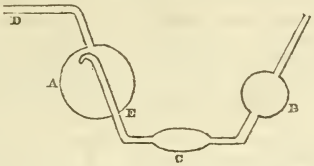
In order to overcome this difficulty, those chemists recommend, in the analysis of substances rich in nitrogen, the addition of a quantity of sugar, in order that the gases disengaged by its combustion may dilute the ammoniacal vapours, and so prevent the absorption from becoming too rapid. One objection that applies to this addition of sugar is, that a larger quantity of the mixture of soda and lime will be required to ensure the complete combustion of the body which is being analysed, and another is the possible introduction of some nitrogenous substance in the sugar employed.

Having been lately engaged in conducting a number of such analyses, I made an alteration in the form of the tube, which prevents regurgitation taking place, and renders the operation much more easily performed than with the original apparatus.

The form will be seen from the annexed sketch. The tube proceeding from C, instead of terminating at the point E, as in the original form of the apparatus, is continued nearly to the top of the ball A, and curved downwards, the joining at E being made when the tube is formed by the glass-blower. This form of tube is made

* Communicated by the Author.

of the usual size, and is filled with the acid in the same way as in using the old form, with this slight difference, that only a very few



drops of the acid should be introduced into the ball A. At the end of the combustion, when absorption of the gases contained in the combustion-tube takes place, the acid liquid flows tranquilly from the balls C and B into A without any of it reaching the combustion-tube. From the above explanation, it will be seen that the ball A must be made sufficiently large to contain rather more than the whole of the acid used in the analysis.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Detection of Cotton in Linen. By G. C. Kindt.

This subject has frequently engaged the attention of commercial and scientific men; many experiments have been made in order to detect cotton thread in linen; many processes have been recommended, but none have hitherto proved satisfactory. I was therefore much surprised when a stranger, a few weeks ago, showed me a sample of linen from the one-half of which all the cotton filaments had been eaten away. He had obtained it in Hamburg, and asked me whether I could give him a process for effecting this purpose. Now since, as far as I am aware, nothing has been published on this subject, and it is of very general interest, I consider it a duty to communicate the results of my experiments. I had already observed, in experimenting with explosive cotton, flax, &c., that these two substances behave somewhat differently towards concentrated acids; and although it has long been known that strong sulphuric acid converts all vegetable fibre into gum, and when the action is continued for a longer period, into sugar, I found that cotton was metamorphosed much more rapidly by the sulphuric acid than flax. It is therefore by means of *concentrated sulphuric acid* that cotton may be removed from linen when mixed with it; and this object may be obtained by the following process:—

The sample to be examined must be freed as perfectly as possible from all dressing by repeated washing with hot rain- or river-water, boiling for some length of time, and subsequent rinsing in the same water; and I may expressly observe, that its entire removal is requisite for the experiment to succeed. When it has been well dried, the sample is dipped for about half its length into common

oil of vitriol, and kept there for about half a minute to two minutes, according to the strength of the tissue. The immersed portion is seen to become transparent. It is now placed in water, which dissolves out the gummy mass produced from the cotton; this solution may be expedited by a gentle rubbing with the fingers; but since it is not easy to remove the whole of the acid by repeated washing in fresh water, it is advisable to immerse the sample for a few instants in spirits of hartshorn (purified potash or soda have just the same effect), and then to wash it again with water. After it has been freed from the greater portion of the moisture by gentle pressure between blotting-paper, it is dried. If it contained cotton, the cotton threads are found to be wanting in that portion which had been immersed in the acid; and by counting the threads of the two portions of the sample, its quantity may be very readily estimated.

If the sample has been allowed to remain too long in sulphuric acid, the linen threads likewise become brittle, or even eaten away; if it were not left a sufficient time in it, only a portion of the cotton threads have been removed; to make this sample useful, it must be washed, dried, and the immersion in the acid repeated. When the tissue under examination consists of pure linen, the portion immersed in the acid likewise becomes transparent, but more slowly and in a uniform manner, whereas in the mixed textures the cotton threads are already perfectly transparent, while the linen threads still continue white and opake. The sulphuric acid acts upon the flax threads of pure linen, and the sample is even somewhat transparent after drying as far as the acid acted upon it, but all the threads in the sample can be seen in their whole course.

Cotton stuffs containing no linen dissolve quickly and entirely in the acid; or if left but one instant in it, become so brittle and gummy that no one will fail to recognise it as cotton when treated in the above manner.—Liebig's *Annalen*, Feb. 1847.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Jan. 18, 1847. (John Thomas Cooper, Esq., Vice-President, in the Chair.)

"Note on the Action of a Solution of Caustic Soda upon a Stoneware Jar," by Mr. Trenham Reeks.

The author's attention was drawn to this subject from the presence of a large quantity of alumina in the analyses of some bronzes and iron ores. On examining the reagents employed, it was found that it originated in the soda, which had been kept for some time in a stoneware jar, the alumina of which had been dissolved out by the soda, and a thick coating of silica left closely adhering to its surface. A portion of this jar was exhibited.

Mr. Thomas Taylor described some improvements in the form of chemical apparatus which he had been in the habit of using. The first was a method of closing the mouths of bottles intended for the

preparation of gases. It consists in first slightly grinding the top of the bottle so as to obtain a level surface, and introducing a piece of sheet caoutchouc between this and a disc of wood of the size of the top of the bottle, which is kept tight down by means of a small cross bar having a tightening screw through its centre, and with corks which pass under the rim of the neck; through this wooden top the tubes required pass into the bottle, and are cemented. If small bottles are used, a string tied tight over the top and round the neck is sufficient.

The second is a convenient mode of cupelling, and consists in forming a substitute for the muffle by two black-lead pots, the mouths ground flat to each other, and having in the upper one an orifice at the end turned upwards, and a semicircular opening made at the top or lower edge. When used, the lower pot is to be nearly filled with sand, and placed on the bars of the furnace, and brought to a low red heat; the cupel, with the material under examination, is then introduced, and covered with the other crucible, taking care that the side-opening is opposite the door of the furnace. The heat having been raised, the furnace-door is opened, and the fuel gently moved from before the semicircular aperture, so as to admit the air. Cupels may be constructed in this way of the same diameter as the crucibles used.

The third consists in an enlargement of Will's nitrogen apparatus to about three times its size, and the surmounting two additional bulbs, with a wide communication, on those generally used.

Mr. Taylor also exhibited a small instrument he had constructed for holding the plates, in the Daguerreotype process, during the washing-off, and which he had found very serviceable.

Feb. 1, 1847. (James Lowe Wheeler, Esq., in the Chair.)

Dr. Playfair communicated a discovery made by Mr. Mercer of the Oakenshaw Print Works, Lancashire, of the power of caustic potash, soda and ammonia to discharge indigo blue in the presence of red prussiate of potash. The simplest explanation seems to be that red prussiate of potash, $Fe^2 Cy^6 3K$, has a great affinity for an additional atom of K, in order to pass into $F^2 Cy^6 4K$, or yellow prussiate of potash, the oxygen at the moment of its liberation removing the colouring matter. This action was interesting from its theoretical consequences, and seemed to show that the red and yellow prussiate both contain the same radical, differing only like phosphoric acid, which is according to circumstances either tribasic or bibasic. $Fe^2 Cy^6$ would thus exist both in ferrocyanogen and ferricyanogen, the only difference being that one is quadribasic, the other tribasic. Red prussiate of potash and the alkalies form a powerful means of oxidizing. The fact that ammonia acts as potash and soda in the action is much in favour of the ammonium theory, being much more easily explicable on this view than on the supposition that it is an amide of hydrogen, $N H^2 H^3$.

"On a Process for estimating the Value of the Materials used for the Operation of Tanning," by Robert Warington.

This process consists in employing a test liquor of gelatine of such strength that each measure of 10 grs. in the ordinary alkalimetry

tube, having the volume of 1000 grs. of distilled water divided into 100 equal parts, shall be capable of precipitating the tenth of a grain of pure tannine. A hot infusion of the material to be examined, in a bruised state if necessary, is to be prepared, strained, and the test gelatine liquor gradually added until no further precipitate is formed. To obtain at intervals portions of the solution under trial in a bright state, so as to be able to ascertain the progress of the operation, a glass tube having an internal diameter of about half an inch is employed, having the lower orifice loosely closed by a small piece of wet sponge; this, from the curdy nature of the precipitate, on being immersed allows the clear liquor to filter through the sponge by ascent, and the filtrate is then to be poured into a small test-glass, and acted upon by an additional quantity of the solution of gelatine; if this renders it turbid, it is decanted back to the original bulk, and the process continued. In this way great accuracy may be arrived at after a little practice.

Royal Institution.

Friday, March 19, 1847.

(Admiral Sir E. Codrington, Vice-President, in the Chair.)

"On the Raising and Shaping Metal by Stamping and Pressure," by Mr. Carpmael.

Mr. Carpmael's purpose was to show how objects of extreme perfection of workmanship and of great use in daily life are produced by simple manipulation. Having adverted to the old process of stamping sheet metal, and remarked that this process generally required that the article stamped should have a flange or rim, and that the process was inapplicable to any ornamental work which required undercutting in the sculptured part, Mr. Carpmael proceeded to describe the improvement lately introduced by what is technically termed *spinning* (*i. e.* burnishing to form). This operation is performed by fixing the object in a lathe and pressing its surface with a blunt tool. Mr. Carpmael explained how, by means of a divided mandril, undercut forms could be obtained. He then pointed out that this burnishing to form could be alternated with *casting*, and that the flange was rendered unnecessary in the casting process, the metal being driven through a conical mould, much on the principle on which pipes, &c. are drawn; the difference being that in the process which Mr. Carpmael was describing the object was forced through the gradually-contracting aperture by the blow of a heavy weight falling on its lower surface. The effect of these combined operations was not only to produce ornamental articles, but also others of utility, and at a low price. Of the latter, Mr. Carpmael presented an example in a tea-pot, made of tinned iron-plate by the joint process of *casting and burnishing to form*. This article, which he affirmed to be of the best fabric, is sold (wholesale) for 1*s.* 8*d.* In conclusion, Mr. Carpmael exhibited the machines by which tin is shaped into boxes and bottles for holding colours, perfumes, &c., by squeezing a small ingot of this ductile metal by a powerful pressure.

THE CHEMICAL GAZETTE.

No. CVIII.—April 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of the so-called Sulphocyanogen, and on a new Acid of the Mellon Series containing Sulphur. By A. Jamieson.

When the so-called sulphocyanogen, produced by the action of chlorine upon the sulphocyanide of potassium, is boiled with water, a distinct odour of sulphuretted hydrogen is perceptible, and hydrosulphocyanic acid, together with a small quantity of a yellow body containing sulphur, pass into solution, while the greater portion of the sulphocyanogen is left undissolved. By repeating this operation as long as boiling water dissolves anything, a pure yellow powder remains, which yielded the following results on analysis:—

Carbon....	19·10	19·24	..	..	4	= 300	19·04
Nitrogen ..	22·28	22·44	..	..	2	350	22·22
Sulphur ..	..	..	50·88	..	4	800	50·80
Hydrogen	1·56	1·60	..	..	2	25	1·58
Oxygen ..	..	..	..	..	1	100	6·36

This body may therefore be viewed as consisting of—

1 equiv. sulphocyanogen	$C^2\,N\,S^2$
1 equiv. hydrosulphocyanic acid	$C^2\,N\,S^2\,H$
1 equiv. water	$H\,O$
	$C^4\,N^2\,S^4\,H^2\,O$

or as hydrosulphocyanic acid with half the amount of hydrogen combined with 1 equiv. water.

Sulphocyanogen dissolves readily in the sulphuret of potassium and hydrogen with evolution of sulphuretted hydrogen. The filtered solution yields, on the addition of acetic acid, a yellowish precipitate, consisting of an acid containing nitrogen and hydrogen. It is best obtained by adding sulphocyanogen to a tolerably concentrated solution of the sulphuret of potassium and hydrogen until the liquid takes up no more even on boiling. Small quantities of a brown body always remain undissolved in this operation, and a considerable quantity of sulphocyanide of potassium is found in the liquid. The filtered solution is kept boiling from 10 to 12 hours, when it is allowed to cool, and then neutralized with acetic acid. This pro-

duces an abundant precipitate, consisting of the acid and a large quantity of sulphur; a portion of the acid remains in solution, and may be obtained by evaporation. To prepare the acid pure, the precipitate is well-washed with water, and then treated in the cold with aqueous ammonia, which dissolves the acid and leaves almost the whole of the sulphur undissolved. The filtered liquid is placed in a warm spot until every trace of sulphuret of ammonium has disappeared, and then boiled with animal charcoal until a snow-white precipitate is formed upon the addition of a mineral acid. The acid is scarcely soluble in cold and sparingly in boiling water, from which it crystallizes on cooling in very minute white acicular crystals. It is also nearly insoluble in alcohol and æther; it is perfectly tasteless, and has an acid reaction; when heated it is decomposed into sulphuretted hydrogen and mellon; the decomposition begins even between 284° and 302°, but is completed at a higher temperature. Heated with muriatic and sulphuric acid, it yields sulphuretted hydrogen and cyanuric acid; when heated with nitric acid, it likewise gives cyanuric acid. When chlorine is passed through a solution of the potash salt of this acid, a white precipitate is formed, which has not yet been examined. The acid yielded on analysis—

Carbon....	22·60	22·51	..	..	6 =	450	22·50
Hydrogen..	2·69	2·68	..	..	4	50	2·50
Nitrogen ..	35·15	35·02	..	..	4	700	35·00
Sulphur ..	..	..	39·99	39·88	4	800	40·00

The acid may be regarded as a combination of mellon with sulphuretted hydrogen, on which account the author has called it *hydrosulphomellonic acid.* All its salts contain 1 equiv. metallic oxide to 1 equiv. acid; the salts with alkaline bases are soluble in water and alcohol, and separate in beautiful crystals capable of measurement; the acid likewise forms crystalline salts with several of the true metallic oxides.

Sulphomellonide of Potassium was prepared by dissolving the acid in a tolerably concentrated warm solution of potash as long as the liquid took up any. The filtered solution yielded on cooling an abundant crop of colourless prisms, belonging to the prismatic system, with a vitreous lustre. They dissolve with the greatest ease in water and in alcohol. The salt dried at 248° is decomposed at a higher temperature into sulphuret of ammonium, prussic acid, and a residue soluble in water, from which muriatic acid throws down a gelatinous precipitate. The author found on analysis 11·73 water and 19·70 per cent. potassium; the formula of the salt is accordingly $C^6 N^4 S^4 H^3 K + 3HO$.

Sulphomellonide of Sodium is prepared in the same manner as the potassium salt; it crystallizes in broad transparent tablets with a fatty lustre; but when cooled quickly, it is obtained in small laminæ with a nacreous lustre, resembling cholesterine. Analysis yielded 12·66 per cent. sodium and 12·89 water, corresponding to the formula $C^6 N^4 S^4 H^3 Na + 3HO$.

Sulphomellonide of Barium.—The best method of obtaining this

salt is to boil finely-pulverized carbonate of baryta with hydrosulphomellonic acid until no more carbonic acid is given off, when the liquid is filtered and evaporated. The salt is thus obtained in colourless acicular crystals, with a brilliant diamond lustre; they dissolve very readily in water, and possess the following composition:—

Carbon	16·04	6 =	450·0	15·81
Nitrogen	23·90	4	700·0	24·60
Sulphur	28·21	4	800·0	28·11
Hydrogen	1·43	3	37·5	1·32
Barium	30·45	1	856·9	30·16
Dry salt	100·03	1	2844·4	100·00
Water	16·63	5	562·5	16·50
Crystalline salt	..	..	3406·9	

Sulphomellonide of Strontium is prepared in the same manner as the barium salt. It crystallizes in large transparent tablets of a waxy lustre, which belong to the pyramidal system, and contain 14·95 per cent. water and 20·80 strontium; corresponding therefore to the formula $C^6 N^4 S^4 H^3 Sr + 4HO$.

Sulphomellonide of Calcium.—This is obtained in the same manner as the barium salt, in colourless crystals of a vitreous lustre, with the form of axinite; belonging therefore to the prismatic system. Its formula is $C^6 H^4 S^4 H^3 Ca + 2HO$.

Sulphomellonide of Magnesium.—This salt is likewise readily obtained by the method directed for the barium salt; it crystallizes in minute needles of a vitreous lustre, and is, like the other salts, readily soluble in water. Its formula is $C^6 N^4 S^4 H^3 Mg + 6HO$.

Sulphomellonide of Silver.—When nitrate of silver is added to a solution of hydrosulphomellonic acid in ammonia, a voluminous white flocculent precipitate is obtained, which is perfectly insoluble in water, is not blackened by exposure to the light, and bears a temperature of 212° without being decomposed. It gave on analysis—

Carbon	13·55	6 =	450·0	13·48
Nitrogen	21·07	4	700·0	20·97
Sulphur	24·01	4	800·0	23·97
Hydrogen	1·31	3	37·5	1·12
Silver	40·67	1	1350·0	40·46

Liebig's *Annalen*, lix. p. 339.

On Sulphophosphoric Acid, and on the Oxychloride of Phosphorus. By Ad. Wurtz.

Sulphophosphoric Acid.—I obtained this acid in combination with soda, with which it forms a well-defined salt. It is prepared in the following manner:—The chlorosulphuret of Serullas is treated with a large excess of a moderately-strong solution of caustic soda, the whole conveyed into a retort, and heated in the water-bath. When all the chlorosulphuret has disappeared, the liquid is allowed to cool, when it generally solidifies in the course of a day. The mother-ley

is drained from the crystals, which are then rinsed with a little cold water; they are very easily purified by recrystallization. The following equation explains the reaction which occurs in this operation:—$P(Cl^3 S^2) + 6NaO = P(O^3 S^2), 3NaO + 3ClNa$.

I was not able to isolate the sulphophosphoric acid, for in the free state it is decomposed with great facility, even at the ordinary temperature, into sulphuretted hydrogen and phosphoric acid.

The sulphophosphate of soda is very soluble in boiling water, and is deposited on cooling in the form of very brilliant hexagonal tablets, which effloresce in the dry air, are insoluble in alcohol, and consist, according to my analysis, of $PO^3 S^2, 3NaO + 24HO$. Sulphophosphoric acid is consequently tribasic, like the ordinary phosphoric acid. The solution of the soda salt is very alkaline, like that of the corresponding phosphate. Chlorine, bromine and iodine instantly decompose it, eliminating sulphur and combining with a portion of the sodium; the liquid becomes acid, and a phosphate is formed, as seen by the following equation:—

$$PO^3 S^2, 3NaO + 2Cl = PO^5, NaO + 2ClNa + S^2.$$

Even very dilute nitric acid acts in an analogous manner; it converts the sulphophosphate into phosphate, and sulphur is deposited. The non-oxidizing acids decompose the sulphophosphate of soda by setting the sulphophosphoric acid free; on boiling the liquid, this latter is decomposed into sulphuretted hydrogen and phosphoric acid.

The sulphophosphate of lead is white at the moment of its precipitation, but in the course of a few hours becomes black, and is converted into sulphuret of lead and phosphate, while the liquid has an acid reaction; this decomposition is instantly effected at 212°.

Oxychloride of Phosphorus.—To prepare it in an advantageous manner, it suffices to leave some perchloride of phosphorus in a flask, badly stoppered or furnished with a long neck, in which at the same time a tube containing water is introduced. In this manner the perchloride is always exposed to an atmosphere of aqueous vapour, and gradually dissolves to a liquid, continually disengaging hydrochloric acid. The reaction is represented by the equation

$$PCl^5 + 2HO = P(Cl^3 O^2) + 2HCl.$$

As soon as the perchloride has disappeared, the liquid is distilled, taking care to throw away the first portions, which contain a large excess of hydrochloric acid. The boiling-point rapidly ascends to 230°, when it remains constant, and the oxychloride distils over. In the pure state it is a colourless highly-refractive liquid, of an irritating odour, resembling that of the perchloride of phosphorus. Its density is 1·7 at 54°. When exposed to the air it diffuses white vapours; placed in contact with water, it at first subsides to the bottom of the liquid, and then dissolves with disengagement of hydrochloric acid and formation of phosphoric acid. Its formula is $P(Cl^3 O^2)$. The density of its vapour is 5·40.

If we glance at some of the compounds of phosphorus, we cannot fail to recognise the very intimate relations by which they are con-

nected. It appears to me, that in taking the perchloride of phosphorus as a starting-point, we may form a series, all the terms of which belong to the same type, and some of which are derived from one another in the most direct manner. We have, for instance—

PCl^5	Perchloride of phosphorus.
$P(Cl^3\ S^2)$	Chlorosulphuret of M. Serullas.
PS^5	Persulphuret of phosphorus.
$P(Cl^3\ Br^2)$	Chlorobromide of M. Cahours.
$P(Cl^3\ O^2)$.....	Oxychloride of phosphorus.
$P(Cl^3\ Ad^2)$?	Chloramidide of phosphorus of M. Gerhardt.
PO^5, 3HO	Phosphoric acid.
$P(O^3\ S^2)$, 3HO ..	Sulphophosphoric acid.
PHO^4, 2HO	Phosphorous acid.
$PH^2\ O^3$, HO	Hypophosphorous acid.

I have made several experiments with a view to complete this series. I attempted to prepare the chloroiodide, $PCl^3\ I^2$, and the chlorocyanide, $PCl^3\ Cy^2$, but with negative results.—*Comptes Rendus*, Feb. 22, 1847.

Alteration of the Hydrated Peroxide of Iron under Water. *By* Dr. C. G. Wittstein.

The precipitate obtained from the persulphate or permuriate of iron by ammonia dissolves in the fresh state readily in acetic acid; but if it be kept for any length of time under water, it loses this property almost entirely. If the fresh and well-washed precipitate be examined under the microscope, it appears to consist of amorphous globules without any trace of crystalline structure; a precipitate which has been preserved for a long time under water appears to be altogether crystalline. The time which the precipitate requires for this change cannot now be accurately stated, but it appears to amount to from 1 to 2 years. By the alteration which the hydrated oxide of iron undergoes, it loses half the amount of its water, and is then only $2Fe^2\ O^3 + 3HO$. From the more sparing solubility of the hydrated oxide of iron which has undergone this change, the author recommends not preserving it as a remedy against arsenic beyond a year, but to dissolve it in muriatic acid, and again precipitate it with ammonia.—Buch. *Rept.*, xliii. p. 366.

On some new Compounds of the Cyanide of Mercury. *By* M. Poggiale.

The cyanide of mercury possesses, like the perchloride, electronegative properties, and readily combines with bromides, iodides, chlorides, and even with oxysalts, of which hitherto however but few have been described. They are mostly obtained by adding the cyanide of mercury to a cold saturated solution, for instance, of a chloride, filtering and evaporating the liquid at a very gentle heat; sometimes, in order to obtain beautiful crystals, the evaporation

must be effected *in vacuo*. For analysis, the liquid, acidified with muriatic acid and slightly warmed, was saturated with sulphuretted hydrogen gas. The combination of sulphuret of mercury with cyanide of mercury, which first forms, is converted by the continued action of the sulphuretted hydrogen into pure sulphuret of mercury. In most cases the other salt could be obtained by merely evaporating and igniting the liquid filtered from the sulphuret of mercury. The amount of water in the salt was partly determined by heating them gently on the sand-bath, and partly by drying them *in vacuo*, or over concentrated sulphuric acid.

Cyanide of Mercury with Chloride of Ammonium is obtained by dissolving both substances and slow evaporation; it crystallizes in long needles, which dissolve more readily in hot than in cold water, and become opake by exposure to the air. When heated, the salt is decomposed, and disengages carbonic acid, cyanogen, mercury, and vapours of chloride of ammonium. Muriatic and sulphuric acids disengage prussic acid from it; the latter, at an elevated temperature, cyanogen, sulphurous, carbonic and muriatic acids; the formula of the salt is $2HgCy + NH^3 HCl$. When the mother-ley of the above salt is allowed to evaporate slowly, shining trilateral laminæ of a salt are obtained, with the formula $HgCy + 2NH^3, HCl$.

Cyanide of Mercury with Chloride of Sodium crystallizes in beautiful transparent needles, which contain no water of crystallization. The salt dissolves readily in water, especially in boiling, but little in alcohol. It has the formula HgCy, NaCl.

Cyanide of Mercury and Chloride of Barium.—This salt forms beautiful four-sided transparent prisms, which are abruptly terminated at the extremities, and effloresce in the air, without however crumbling to dust. They very readily part with their water of crystallization when heated, and at a very high temperature they are decomposed. A precipitate is produced by sulphates, by soluble carbonates, and by sulphuretted hydrogen. The formula is—

$$HgCy + BaCl + 4HO.$$

Cyanide of Mercury and Chloride of Strontium.—On the spontaneous evaporation of a mixture of 2 equivs. cyanide of mercury and 1 equiv. chloride of strontium, groups of minute silky prisms separate, which dissolve very readily in water, and lose their lustre after a few hours' exposure to the air. This salt is decomposed, like the preceding, by sulphates, carbonates and sulphuretted hydrogen. Its formula is $2HgCy + SrCl + 6HO$.

Cyanide of Mercury and Chloride of Calcium.—When 1 equiv. chloride of calcium is added to 2 equivs. cyanide of mercury, a salt crystallizes in small prismatic needles on evaporation, which dissolves readily in water and effloresces in the air. Its formula is—

$$2HgCy + CaCl + 6HO.$$

Cyanide of Mercury and Chloride of Magnesium.—This salt crystallizes in prismatic needles, and deliquesces in a moist atmosphere. It contains $2HgCy, MgCl + 2HO$.

Cyanide of Mercury and Protochloride of Manganese.—A solu-

tion of 1 equiv. chloride of manganese and 1 equiv. cyanide of mercury yields on spontaneous evaporation transparent, colourless, four-sided prisms, which are readily soluble in water and effloresce in the air. They consist of $HgCy, MnCl + 3HO$.

Cyanide of Mercury and Chloride of Zinc crystallizes in four-sided columns, which dissolve in water and effloresce in the air. They consist of $2HgCy, ZnCl + 6HO$.

Cyanide of Mercury and Chloride of Nickel crystallizes with difficulty. It is bluish-green and deliquescent. Its formula is probably $HgCy, NiCl + 6HO$.

Cyanide of Mercury and Chloride of Cobalt.—This salt crystallizes in warty yellowish-red aggregations, which become red and effloresce on exposure to the air. The concentrated solution of the salt is blue; the dilute, red, like the chloride of cobalt. The formula is $HgCy, 2CoCl + 4HO$.

Cyanide of Mercury and Chloride of Mercury.—To obtain this combination, 1 equiv. cyanide and 1 equiv. chloride are dissolved in water, and the filtered liquid evaporated at a gentle heat; on cooling, semitransparent four-sided pyramids are obtained, which are not altered by exposure to the air, and dissolve in water. The formula is $HgCy, HgCl$.

Perchloride of Tin appears to combine with cyanide of mercury, but no distinct crystals could be obtained; the protochloride decomposes the cyanide of mercury very rapidly, yielding a gray precipitate of oxide of tin and mercury, and a lively evolution of prussic acid.

Cyanide of Mercury and Iodide of Calcium crystallizes in beautiful silky needles, is very soluble, effloresces, and consists of—

$$2HgCy, CaI + 6HO.$$

Cyanide of Mercury and Formiate of Ammonia crystallizes in four-sided prisms at 392°; it is decomposed into water, hydrocyanic acid and cyanide of mercury; with sulphuric acid it disengages when heated carbonic oxide. It consists of $HgCy, C^4 H^2 O^3, NH^3$.

Cyanide of Mercury and Chromate of Potash.—This combination has already been prepared by Caillot and Poitevin, but not yet analysed. It crystallizes in laminar needles, is soluble in water, is not altered by exposure to the air, and takes fire at a higher temperature. According to the author its formula is $2HgCy, KO, CrO^3$.—*Comptes Rendus*, xxiii. p. 762.

On a Combination of Oxide of Bismuth, Potash and Tartaric Acid. *By* A. Schwarzenberg.

Oxide of bismuth, obtained by digesting the basic nitrate with caustic potash, was boiled with bitartrate of potash, taking care to have an excess of oxide always present; the filtered solution forms a clear heavy liquid, which is precipitated like tartar-emetic by strong mineral acids, but it is not rendered turbid by water. This solution was concentrated in the water-bath, when it deposited a

heavy crystalline powder of a pure white colour. This powder is decomposed by water, yielding an acid liquid, which only after very long standing passed clear through the filter; the clear liquid contained no bismuth. The substance, dried in a water-bath and burnt with chromate of lead, exhibited the following composition:—

	Found.	Calculated.
Carbon	12·16	12·06
Hydrogen	0·59	0·50
Oxygen	16·09	16·09
Oxide of bismuth	58·94	59·52
Potash	12·22	11·83

leading to the formula $C^8 H^2 O^8 + BiO^3, KO$. This therefore corresponds with the tartar-emetic dried at 374° F.—Liebig's *Annalen*, Feb. 1847.

On the Equivalent of Titanium. *By* J. Pierre.

To determine the equivalent of titanium, the author employed the method proposed by Gay-Lussac for the analysis of the alloys of silver, and employed by M. Pelouze in investigating the atomic weights of several simple bodies, in particular of phosphorus, nitrogen, arsenic and silicium. From the facts detailed by the author, it results that the equivalent of titanium is much higher, for the author proposes substituting the number 314·69 for that generally adopted according to the experiments of H. Rose, viz. 303·686.—*Comptes Rendus*, March 8, 1847.

Observations on Creatine. *By* M. Heintz.

About two years ago I described a peculiar substance which I had discovered in the normal urine of man. From subsequent investigations I find that this substance is identical with that which M. Chevreul found in meat broth, to which he gave the name of creatine, and the presence of which in the fresh muscular flesh of different animals has recently been shown by Liebig*.

The most advantageous method of procuring the substance is that subsequently pointed out by M. Pettenkofer; it consists in adding to the alcoholic extract of the urine an alcoholic solution of chloride of zinc; in a short time a deposit is formed, which contains the creatine in combination with the chloride of zinc, together with a small quantity of phosphate of zinc. These two substances are separated by boiling water, which dissolves the first, but is without action upon the latter. The pure creatine is obtained from the aqueous solution of its combination with chloride of zinc by precipitating the zinc with hydrosulphate of ammonia; after having evaporated the filtered liquid as far as possible without a precipitate being formed in the boiling solution, absolute alcohol is added to it, when the creatine is immediately deposited in the form of small crystals,

* See pp. 81 and 112 of the present volume.

resembling those obtained in operating upon the alcoholic solution of the aqueous extract of meat.

After having washed these crystals with alcohol, I recrystallized them from water. The elementary analysis of the pure crystals led to the following formula, $C^8 H^9 N^3 O^4 + 2HO$, which is the same as that advanced by M. Liebig.

When creatine enters into combination with chloride of zinc, it parts with 2 atoms of water besides the water of crystallization, and in exchange takes up 1 atom of this salt. This combination is represented by the following formula, $C^8 H^7 N^3 O^2 + ClZn$, and the atomic weight of creatine is consequently 1412·5.

From the experiments of M. Liebig it results, that of all the organs of the animal body it is only the muscles which yield creatine. Now, as I have proved its presence in the urine of man and animals, it appears placed beyond all doubt that this substance is formed in the muscles, that it is absorbed by the lymphatics or blood-vessels, and is finally secreted by the kidneys, like urea, &c. We may therefore conclude that creatine should henceforth be placed amongst the *excrementitious* substances; and consequently it is barely probable that it constitutes one of the most important alimentary principles of meat broth, as M. Liebig is inclined to think. Is it not rather one of the ultimate products of the chemical actions, the presence of which we have great reason to suspect in the act of muscular contraction?—*Comptes Rendus*, March 22, 1847.

On the Composition of the Essential Oil of Thyme (Thymus vulgaris). *By* L. Doveri.

The essential oil of thyme is composed of two distinct oils, one of which boils at 356°, the other at 455°. The composition of the first may be expressed by the formula $C^{34} H^{26} O$, that of the second by $C^{40} H^{30} O^7$; the density of its vapour is 5·511. This last oil is dehydrated when submitted to the action of anhydrous phosphoric acid; but while it readily parts with its 2 first equivalents of water, it is extremely difficult to remove the 2 last; however, after several distillations over anhydrous phosphoric acid, it is converted into a carburetted hydrogen, the composition of which agrees with the formula $C^{40} H^{26}$.—*Comptes Rendus*, March 8, 1847.

On a Method of detecting the admixture of Phormium tenax, *or New Zealand Flax, with the Hemp and Flax of European growth and Preparation. By* M. Vincent.

It appears that the *Phormium tenax* does not possess certain qualities essential for naval cordage, and it was considered important to discover the means of detecting the presence of this article. M. Vincent has found that if the *Phormium tenax* be immersed in pure nitric acid, its fibres, owing to the presence of some azotic substance, assume a blood-red tint; which is not the case with the hemp and flax admitted for use in the navy. Thus it is very easy, by sub-

jecting a rope to the action of nitric acid, to discover whether there has been any admixture of *Phormium tenax*. The Report of the Committee confirms the statement of M. Vincent.—*Comptes Rendus.*

ANALYTICAL CHEMISTRY.

On the Examination of the Ashes of Organic Bodies. By H. Rose.

Considerable attention has recently been paid to the analysis of the ashes of plants and animal substances. We now possess a very large number of quantitative analyses of different ashes, which may considerably enlarge our knowledge of the chemical composition of the inorganic constituents of organic substances. Frequently, however, very incorrect conclusions are liable to be drawn from the results of these analyses, as they have hitherto been made, with respect to the constituents in the organic body. This observation struck me on perusing M. Enderlin's paper*, who found in the ashes of the blood only phosphate of soda ($3NaO + P^2O^5$), phosphate of lime and magnesia, peroxide of iron and perphosphate of iron, sulphate of soda, sulphate of lime, chloride of sodium and potassium, but no alkaline carbonates. From the results found he asserted the total absence of carbonated alkalies and of alkaline salts with organic acids in the blood. It is evident, however, that these conclusions may be erroneous, in so far as at a high temperature the ordinary phosphate of soda ($2NaO + HO + P^2O^5$) is capable of expelling the carbonic acid from the carbonate of soda and forming basic phosphate of soda.

This observation, respecting the conclusions which M. Enderlin has drawn from his investigations, has already been made by several persons. Marchand† has attempted to refute Enderlin; Berzelius, in his most recent report, likewise draws attention to the subject; and Golding Bird‡ has prepared the basic phosphate of soda ($3NaO + P^2O^5$) by heating the ordinary phosphate of soda ($2NaO + HO + P^2O^5$) to redness with acetate of soda.

I have also examined the ashes of the blood (ox-blood), but have obtained very different results from those of M. Enderlin. The process I adopted was the following:—I exposed the blood in a covered platinum crucible to a very faint red heat, extracted the cold mass with water, and evaporated the colourless liquid to dryness; it consisted of alkaline chlorides and carbonates, with very minute quantities of alkaline sulphates and phosphates. The charred mass, extracted with water, was now treated with hydrochloric acid; the filtered solution did not yield with ammonia a very considerable precipitate, which, although it looked almost like pure hydrated oxide of iron, contained some phosphoric acid as well as lime and magnesia. In the filtered solution, I obtained with oxalate of am-

* Chem. Gaz., vol. iii. p. 230.

† *Ibid*, vol. iv. p. 209.

‡ Phil. Mag., vol. xxvi. p. 532.

monia a pretty considerable precipitate of oxalate of lime, proving the presence of carbonate of lime in the charred blood; and in the liquid separated there was also a small quantity of magnesia. The cinder, after treatment with water and hydrochloric acid, yielded a very considerable quantity of a red-coloured ash on being burnt in an atmosphere of oxygen. It was in a semifused state, and contained peroxide of iron (which formed the chief part), earthy and alkaline phosphates*.

If the fixed constituents in plants are examined according to the above process, totally different results are frequently obtained to those yielded by the ash analyses which have been published up to this time. The ashes of peas have been examined by Fresenius and Will, Bichon, Thon and Boussingault; none of them enumerate carbonic acid among the constituents. From the investigations which have been made by Drs. Gibbs and Bromeis in my laboratory, the amount of carbonic acid in the salts which are extracted from the charred peas by water amounts to somewhat more than 27 per cent. Evidently, in the former method of reducing to ash, the carbonic acid has been entirely expelled. Phosphoric acid is only present in small quantity in the aqueous extract of charred peas. When the charred peas are subsequently treated with hydrochloric acid, a solution is obtained which contains a moderate quantity of earthy phosphates. If the charred peas are now perfectly reduced to ash in an atmosphere of oxygen, a very considerable quantity of ash is obtained, which consists principally of earthy and alkaline phosphates.

That the method of preparing the ash of organic substances has considerable influence upon the composition of the ash has already been noticed by several chemists, especially by Erdmann†, who showed that acid phosphates, which yielded white precipitates with nitrate of silver by ignition with carbon, lost a considerable portion of the phosphoric acid, and then produced a yellow precipitate in the solution of silver; he observed further, that chlorine and sulphuric acid might be contained in very different quantities in the ashes, according to the mode of preparing them; and that in the ashes of many seeds not a trace of chlorine had been found, while the aqueous extract of the seed contains very perceptible quantities of chloride of sodium. Mitscherlich‡ has likewise drawn attention to several circumstances, by which, in incinerating organic substances, the ashes are frequently decomposed and rendered impure.

The mode of determining the fixed constituents of an organic substance, as above described, appears to me more advantageous and far more rational than the methods usually employed. It may be objected to it, that it takes more time; but not only are far more correct results obtained by it, but it is also capable of answering several questions as to how or in what combinations the constituents found in the ash were contained in the organic substance. According

* After these observations had been penned, I observed that Lehmann had proved the presence of alkaline carbonate in the blood by a different method.—See *Chem. Gaz.*, p. 133 of the present volume.

† Chem. Gaz., vol. iv. p. 230.

‡ *Ibid*, vol. iv. p. 69.

to the method which I propose, the organic substance is charred at a very faint red heat, so that the water with which it is extracted is not coloured yellowish or brownish. At this temperature, which, owing to the volatilization of so many substances, is much lower than would appear, no alkaline chlorides are volatilized, nor can chlorine be expelled from them in the form of hydrochloric acid by acid phosphates. The alkaline and earthy phosphates are not able to expel the carbonic acid from the alkaline carbonates, either contained in the organic substance or formed by the charring; nor can phosphoric acid be eliminated from its combinations by silica, reduced by carbon, and volatilized in the form of phosphorus. The charring is effected either in a spacious covered platinum crucible over a spirit-lamp, or, with larger quantities of the organic substances, in a spacious covered Hessian crucible, especially if they do not fuse. When there is no longer much empyreumatic odour perceptible, the heating is discontinued, the cold mass left for some time in contact with water, and the solution of the soluble salts furthered by heating; the edulcoration requires considerable time and much hot water; but if the highest degree of accuracy is not desired, the edulcoration may be discontinued when several drops of the wash-water leave a scarcely perceptible residue on evaporation upon a slip of platinum; this point is very soon attained.

The aqueous extract contains the alkaline salts. The alkaline chlorides were contained as such in the organic substance previous to the charring, as well as at least a part of the alkaline sulphates and phosphates. If, as in most cases, carbonated alkali is found in the aqueous extract of the charred mass, it either pre-existed in the organic substance, or the alkali in it was combined with an organic acid or some other organic body, which acted the part of an acid towards the alkali. If the organic substance contain sulphate of lime, this, when carbonated alkalies are present in sufficient quantity in the charred mass, is converted, on treating the latter with water, into carbonate of lime and alkaline sulphate. In the same way, when phosphate of lime is present, a certain quantity of alkaline phosphates is formed from it in the aqueous extract by the alkaline carbonates. Carbonated alkali and phosphate of lime are not perfectly decomposed even by fusion at very high temperatures. The decomposition in presence of much water is likewise imperfect, and the more alkaline phosphate is obtained in the aqueous extract, the more concentrated the solution, the more carbonated alkali it contains, and the longer the charred mass has been digested at an elevated temperature. Alkaline sulphates and phosphates will however be found in far smaller quantities in the aqueous extract of the charred mass than was to be expected from the ash analyses that have been hitherto published. Frequently the two, and especially the latter, are present only when too high a temperature has been employed in the charring. From this however it is evident that the nature of the salts in the aqueous extract may vary somewhat, according to the temperature employed and the longer or shorter digestion of the mass with water. When the charring is effected at

too high a temperature, the greater portion of the carbonated alkalies are decomposed by the earthy phosphates.

The accurate examination of the salts in the aqueous extract is not accompanied with any great difficulties. One circumstance however renders it somewhat less easy; carbonate and phosphate of lime and magnesia frequently dissolve to a considerable extent in neutral solutions of alkaline salts, particularly of alkaline carbonates and phosphates; in the course of time they are deposited from the solutions, especially after the application of heat. When therefore the aqueous extract is evaporated, it frequently becomes somewhat turbid, and deposits small quantities of earthy salts. It should consequently be evaporated nearly to dryness, diluted with water, and the solution set aside for some time; when the earthy salts have subsided, it is filtered, the filtered solution evaporated to dryness, and its weight determined. When there is no alkaline phosphate or sulphate present, the examination is very easy. The quantity of carbonic acid is determined in a suitable apparatus by decomposition with nitric acid; and upon this that of the chlorine by a solution of silver; upon which, after removing the oxide of silver by hydrochloric acid and concentrating the liquid, the potash may be separated from the soda by chloride of platinum. With the presence of alkaline sulphate or phosphate, it is advisable to divide the quantity of the alkaline salts, and in the one half to determine the quantity of the chlorine and the alkalies, and in the other that of the carbonic acid by decomposition with hydrochloric acid; that of the sulphuric acid by a salt of barytes; and after removing the baryta by means of sulphuric acid, and supersaturating with ammonia, to ascertain the quantity of phosphoric acid by means of a solution of a salt of magnesia to which chloride of ammonium has been added.

The charred mass, exhausted with water, is now digested with hot hydrochloric acid for some length of time, and then washed with water. This operation requires considerably more time and water than in the treatment of the charred mass with water; and if the washing were to be continued until some drops of the filtered liquid no longer produced any opalescence in a solution of silver, an enormous length of time, several months, would be required, especially in operating upon large quantities. The edulcoration therefore is only continued until a considerable quantity of the wash-water does not exhibit a trace of precipitate when treated with ammonia; it will then also be seen that a large quantity of the wash-water, when evaporated upon platinum, no longer leaves any perceptible residue; this does not require much time, especially when hot water is used.

The acid solution contains the earthy phosphates which existed as such in the organic substance and the peroxide of iron. It is precipitated by ammonia, and after having determined the weight of the precipitate, the bases are separated from the phosphoric acid. I shall subsequently describe in these pages a method by which this may be accomplished without any difficulty. On separating the earthy phosphates by means of ammonia, a small quantity remains dissolved in the filtered liquid, owing to the presence of chloride of

ammonium; consequently upon adding oxalate of ammonia, a precipitate of oxalate of lime is obtained, but its quantity is usually larger than corresponds to the phosphate of lime dissolved by the chloride of ammonium; consequently a portion of the lime existed as carbonate of lime in the charred mass, or was formed by the decomposition of the sulphate and phosphate of lime by the alkaline carbonates. The liquid filtered from the oxalate of lime indicates, on the addition of a solution of phosphate of soda, the presence of some magnesia. The insoluble earthy salts which separated from the aqueous extract may be examined conjointly with those in the acid extract.

With respect to the charred mass, which has been exhausted with water and hydrochloric acid, it would be imagined that it could contain only silica or silicates undecomposable by dilute hydrochloric acid; but it yields a very large amount of ash on complete combustion, even when the organic substances contain no silica or mere traces.

I formerly effected the perfect combustion of the cinder in hard glass tubes, in which the mass was heated to redness while a current of oxygen was passed over it; this plan however has its inconveniences. If the quantity of organic substance employed is moderately large, so much cinder is obtained, that a glass tube, even of large diameter, would require to be filled with it several times to burn it entirely; moreover, the tube is very much acted upon, and rarely stands a second heating. The combustion is in most cases very imperfect, and requires much time if but a slow current of oxygen be passed; a rapid current is requisite for the combustion to succeed well; but then a considerable quantity of ash may readily be carried away, especially if it is of a very light nature; this, it is true, may be partially prevented by passing the gas on its exit through a stratum of water, by varying the height of which a different pressure may be obtained; but this does not entirely prevent the removal of the ash, and if the pressure is too great, the glass tube is liable to bulge when strongly heated*. But the greatest disadvantage attending the use of glass tubes is, that it is impossible to collect the ashes so as to determine their weight accurately. Frequently the ash has undergone slight fusion; it can then only be imperfectly separated from the glass by mechanical means or the use of solvents. The use of thin platinum or silver foil, which is introduced into the glass tube previous to the coal being placed in it, does not entirely remove these serious disadvantages, and gives rise to others. I therefore employ for the combustion of the charred mass a different method, with the results of which I am perfectly satisfied. For some time past I have no longer employed bulb tubes in reductions by means of hydrogen gas, but place the substance to be reduced in a platinum or porcelain crucible, provided with a platinum lid, which is perforated in the centre, into which passes a curved silver tube about 8 inches long, through which the

* The water employed for this purpose contains cyanogen compounds when the charcoal is derived from nitrogenous bodies.

dried hydrogen is conveyed into the crucible. During ignition the gas escapes between the lid and crucible. Ebelmen* has recently employed a similar apparatus for the reduction of the sesquioxide of manganese to the state of protoxide. This apparatus can be used with considerable advantage for burning the charred mass. The crucible is half-filled with the substance, and heated over a spirit-lamp, while a current of oxygen is passed into it; with proper care not a particle of ash is carried away, and the combustion proceeds very rapidly; a further quantity of the substance is conveyed from time to time into the crucible. By this means the ash obtained may be weighed with such accuracy as would not be easily accomplished in any other way.

When the combustion is effected in a platinum crucible, this is sometimes acted upon; a silver crucible is liable to partial fusion from the heat during the combustion; it is therefore advisable to employ a porcelain crucible, which is acted upon far less than glass; and if very thin and somewhat transparent, the progress of the combustion may be distinctly observed by the incandescence.

The weight of the ash obtained, added to that of the evaporated aqueous extract of the charred mass and to that of the insoluble earthy salts dissolved by the hydrochloric acid, gives the correct quantity of fixed constituents in the organic substance employed.

The ash obtained, especially when derived from vegetable substances, consists of the same constituents as were found in the aqueous and acid extracts; if alkalies were present in them, we likewise find them in the ash of the exhausted charred substance; otherwise it consists principally of earthy phosphates. I have already mentioned that nearly the whole of the iron of the blood is met with in this ash. Only about the tenth part of it is found in the acid extract of the charred mass, and indeed the less the more carefully the charring was effected with exclusion of the air. When the organic substance contains no silica, various views may be entertained respecting the origin of the ash from the charred mass which has been exhausted with water and acid. The most probable is perhaps to derive it from an imperfect exhaustion with the two solvents. When an organic substance is destroyed by heat, the charcoal formed may contain such cavities that the inorganic salts surrounded by them are protected from the action of the solvents. The globules of the blood, those of yeast, the cells of plants, form perhaps after charring extremely minute vesicles, with such small apertures that no liquid can penetrate into them. That the vessels of wood are capable of forming extremely thin filaments with minute apertures by charring is known from the investigations of Degen†. The charred mass of an organic substance (yeast), after it had been most carefully exhausted by water and hydrochloric acid, was ground to the very finest powder upon a plate of agate; the two solvents now extracted only imperceptible traces of fixed constituents, and after burning the exhausted charred mass I obtained the same large amount of ash as from the non-pulverized charcoal. It may nevertheless be supposed

* Chem. Gaz., vol. i. p. 685. † Poggendorff's Annalen, vol. xxxv. p. 468.

that the extremely minute vesicles were not destroyed and torn by the friction upon the agate plate. The microscope threw no light upon the subject.

It is known that charcoal is capable, by a weak kind of affinity, of removing certain salts from their solutions; I have also mentioned above, that when the charred substance has been treated with hydrochloric acid, it is almost impossible to remove the acid by washing with water; but the quantity of ash is too considerable for us to ascribe this origin to it, since it is known that the salts which the charcoal has combined with may be entirely separated by long treatment with water at different temperatures. I mixed sulphate of potash and phosphate of lime with sugar, and charred the mixture. Water, and after this hydrochloric acid, extracted the two salts so completely from the charred mass, that the latter, after combustion in an atmosphere of oxygen, left not a trace of ash.

Several acid phosphates (metaphosphates) are insoluble in hydrochloric acid after ignition; to this cause might be owing the residuary ash of the charred mass; but although phosphoric acid is almost constantly met with in this ash, it is not always combined with the bases in the form of acid salts; moreover, the ash itself, when it does not contain silica, is soluble in hydrochloric acid after the salts have been exposed, in the combustion of the carbon in oxygen, to a far higher temperature than that employed in charring the organic substance.

Ignited peroxide of iron is, it is true, not insoluble in hydrochloric acid, although very sparingly soluble; its non-extraction by acid from the charred blood might be attributed to this cause; but supposing it to be contained in the state of peroxide of iron, not only must it be more readily soluble in hydrochloric acid, owing to its finely divided state, but the oxide of iron which is found in the ash after the combustion of the coal, and which has been exposed to a very high temperature, is soluble in hydrochloric acid.

The alkaline and earthy phosphates which are found in the ash of the exhausted charred mass cannot have been contained in the form of metallic phosphurets of a peculiar kind mixed with coal, like the phosphuret of iron, which is perfectly insoluble in hydrochloric acid. It might be assumed that they were formed by the reduction of the alkaline and earthy phosphates by the carbon. It is scarcely necessary to notice this assumption, for it is well known that the neutral and basic alkaline and earthy phosphates are not reduced by carbon even at a high temperature, at least not in the presence of silica or any similar fixed acid. But even the excess of phosphoric acid cannot be reduced by carbon from the acid phosphates at the temperature which I employ in charring organic substances. In the case of the blood, however, phosphuret of iron might be formed by the reduction of the phosphate of iron by the carbon. Although I was convinced that this could not happen at the temperature which I employed, I mixed phosphate of iron intimately with sugar, and charred the mixture at a higher temperature; hydrochloric acid, however, extracted the salt so completely from

the charred mass, that this burnt without any residue in an atmosphere of oxygen.

It might be supposed that the salts found in the ash of the exhausted charred substances are so intimately combined with organic substances that they can only be detected by reagents after the complete destruction of the latter. But the organic substances are so destroyed by the charring, that if the inorganic salts found in the ash pre-existed as such in them, they should have been extracted by those agents in which they are soluble.

There still remains one view respecting the origin of these ashes. The salts found in them may perhaps not have pre-existed as such in the organic substances, but were first formed by oxidation after the burning of the coal. It has long been known that the proteine compounds, of both animal and vegetable origin, contain sulphur and phosphorus in an unoxidized state; but, as far as I am aware, the supposition has never been advanced, that the radicals of the earths and alkalies may likewise be contained in organic substances in an unoxidized state, perhaps combined with those elements. These would certainly constitute a very peculiar class of combinations, such as we are at present not acquainted with. If they are really combined with organic substances in the living body, they cannot have been essentially altered on destroying the organic body by charring, or they have entered into combinations with carbon and nitrogen, which are insoluble in water and in hydrochloric acid.

I have already observed that the salts found in the ash of the charred mass exhausted with water and acid, especially when derived from vegetable substances, are similar to those which occur in the aqueous and acid extract. This view can only be confirmed by a long series of investigations; but if it should be confirmed, then those salts which we find in the ash after the destruction of the living plants were probably contained in them only in part as such, and in part in an unoxidized state. The inorganic salts, therefore, which are taken up from the soil by the living plant, are partially deoxidized by it, and in this state form combinations with organic substances contained in the plant.

This view is far more probable with respect to several animal substances, especially the blood, than in reference to plants. It has long been suspected that the iron in the blood was contained in it in an unoxidized state; and, according to the recent investigations of Mulder, the iron is actually extracted by acids from hæmatine with evolution of hydrogen gas. This view acquires still greater probability from the experiments which I have related. On the other hand, it is very remarkable that the iron cannot be extracted from the charred blood by hydrochloric acid. I think it would be extremely interesting to pursue this subject further. From what has been stated, it results that the view which I have advanced can neither be confirmed or refuted by any number whatever of analyses of the ashes of plants, which have been prepared according to the methods hitherto in use, but only by a process similar to that I have

described, and which I have therefore pronounced a far more rational method of investigation.

I have already shown that frequently very considerable quantities of alkaline carbonates are extracted by water from several organic substances after charring, in the ashes of which no carbonic acid was found by former investigators. But all organic substances do not yield alkaline carbonates when treated in this manner, even though considerable quantities of alkali are contained in their ash. Highly remarkable in this respect is yeast, the ash of which, according to Mitscherlich *, contains no carbonic acid and no metallic chlorides; and my experiments show that they are likewise not to be found in the aqueous extract of the charred yeast. Yeast diffuses, on being charred, an odour similar to that of the proteine compounds; the aqueous extract did not turn litmus-paper blue, became turbid on evaporation, and deposited a large quantity of earthy phosphates. The mass, evaporated to dryness, yielded on filtration a clear solution, which faintly reddened litmus-paper, and contained therefore not a trace of alkaline carbonates; I could only find in it alkaline phosphates, with very minute traces of alkaline sulphates and chlorides. The charred mass gave, on treatment with hydrochloric acid, a solution, from which ammonia threw down a considerable precipitate of earthy phosphates. The cinder, exhausted with water and acid, furnished on combustion a very large quantity of ash, which contained the same constituents which had been extracted from the charred mass. These experiments, the results of which entirely agree with those obtained by Mitscherlich, were made with top-yeast, which had been perfectly purified by washing. Other results may perhaps be obtained by using unwashed yeast for the experiments; for the beery liquid, separated from the yeast by filtration and evaporated, did not diffuse on charring the same disagreeable odour as the yeast itself, or as nitrogenous substances generally at a high temperature. The evaporated solution, extracted with water from the charred mass, contained a large amount of carbonated alkali, and effervesced therefore strongly with acids, with much chloride of potassium, but only a little phosphate of potash. The charred mass, exhausted with water and hydrochloric acid, yielded a tolerable quantity of a light ash containing phosphates and a large quantity of silica, which latter element Mitscherlich likewise found in the ash of beer †.

* Chem. Gaz., vol. iv. p. 69.

† After this paper had been read before the Royal Academy of Berlin, I received a letter from Berzelius, to whom I had communicated the principal results, in which he states that he advanced a view similar to that which I have proposed on the ashes of the blood, more than 40 years ago, in his work on animal chemistry. It occurs also in Schweigger's 'Journal für Chemie und Physik,' vol. ix. p. 391, 1813. It has however never been expressed in the various editions of Berzelius's 'Manual of Chemistry.'

On the Behaviour of Salts of Cadmium towards Sulphuretted Hydrogen. By Dr. H. Reinsch.

The author had formerly observed that lead and tin are not precipitated from very acid solutions by sulphuretted hydrogen, or not with the usual colour. Cadmium exhibits a similar behaviour, by which it can be distinguished from arsenic. When, for instance, arsenious acid is dissolved in muriatic acid, and sulphuretted hydrogen passed through it, the arsenic is entirely precipitated as sulphuret; on the contrary, a salt of cadmium, dissolved in concentrated muriatic acid, only yields, when the gas has been passed through it for a long time, a white, somewhat pulverulent precipitate, which is a combination of sulphuret of cadmium with chloride. It could not be examined quantitatively, as on edulcoration with water chloride of cadmium is dissolved, and yellow sulphuret is left on the filter. When the solution containing the white precipitate in suspension is diluted with water, it is coloured yellow; but on adding concentrated muriatic acid to it, sulphochloride is again formed; a proof that it can only exist with a certain concentration of the acid. Marsh's test is not at all affected by the presence of cadmium in the zinc, as it does not produce any stain, which happens only with arsenic, antimony and tellurium. When similar results have been obtained with iron, bismuth, &c., it arose from deception, traces of the metals being carried over with the gas, and adhering to the porcelain plate. It is easy to be convinced of this by moistening a plate with a solution of tin, zinc or bismuth, and then passing a flame of hydrogen over them, when metallic mirrors are immediately produced.—*Jahrb. für Prakt. Pharm.*, xiii. p. 72.

PATENT.

Patent granted to Jacque Kloet, Manchester, *for an improved Combination of Materials, to be used as a Substitute for Leather or for Waterproof Cloth.*

This improved combination of materials, to be used as a substitute for leather, or for waterproofing cloth, and other similar purposes, refers chiefly to the preparation of a mixture or cement composed of linseed oil (treated as hereafter described) and a solution of caoutchouc or India-rubber, and other ingredients hereinafter mentioned; which cement may be applied to one or both sides of any cloth or fabric, either manufactured from cotton, wool, or any other fibrous material. The linseed oil to be employed for the above purpose is prepared in the following manner:—Put 20 lbs. of linseed oil and 2 lbs. of coarse bread into a copper vessel of sufficient size to contain 4 times that quantity; the oil is then boiled until the froth or scum is thrown up; and as soon as the bread is observed to rise to the surface of the oil, it must be taken out, and the oil will be found fit for use, the bread having absorbed or taken up all the impurities.

When the oil is sufficiently boiled, add some spirits of turpentine, and then ignite the oil; let it burn about 10 minutes, to evaporate the spirit, and then extinguish the flames. After this, take up some of the oil with a small iron ladle, and let fall a few drops on a piece of flat glass, to see whether it has long threads or fibres; if this proves to be the case, the operation is completed. After the examination close the vessel which contains the oil immediately with a wet woollen cloth, in order to exclude the air; then let it cool, and pour some cold water on it, to prevent the surface from getting dry and unfit for use. The solution of caoutchouc must be prepared as follows:—Take 1 lb. of caoutchouc, cut it in pieces, and boil the same 2 hours in water; after it is well boiled, it must be wiped dry, and cut again into smaller pieces; then add 16 lbs. of spirits of turpentine, and let it stand 5 days or thereabouts in a glazed pan, being careful that the pan is covered, so that no air can get into it. At the expiration of this period, place the solution in a copper vessel, over a slow fire, and boil gently, stirring it frequently with an iron instrument, until the whole of the caoutchouc is dissolved; after which strain the solution, and it is then ready for use.

In employing the above preparation in the manufacture of the improved substitute for leather or for waterproofing cloth, a piece of cloth or other fabric composed of cotton, wool, or other fibrous material, of the required texture and size, must be stretched evenly and tightly in a suitable frame. The dissolved caoutchouc above described, and a little siccative or drying oil, are then spread evenly upon the cloth with a suitable instrument; and after it has been left a day to dry, linseed oil, prepared as above, and afterwards mixed with a small quantity of acetate or sugar of lead and a little drying oil, is applied thereto, by rubbing it well into the cloth, in order to fill up the interstices between the threads of the same. The fabric is then again left to dry. The next operation is to take 1 part of the solution of India-rubber, 1 part of the prepared linseed oil, a little acetate or sugar of lead, and a little siccative or drying oil, and mix the ingredients well together with a little lamp-black; then lay any required thickness of this composition upon the cloth, and wash the surface over with some boiled linseed oil; let it dry again, and afterwards rub the surface well with pumice-stone until it is quite smooth. This done, wipe the surface with some clean linen rags, and let it dry again for a day or two. Then varnish it all over with black varnish (or other suitable colour), and when dry take some very finely-ground pumice-stone, and with a rubber, made of list or other suitable material, rub it over the cloth until it assumes a dull appearance, exactly similar to leather. The operation is then complete, and cloth thus prepared forms the improved substitute for leather, &c.; and when taken from the frame and trimmed at the edges, it is ready for the market. If any other colour than black is required, this may be attained by the introduction of any suitable colouring matter, and the varnish wherewith it is varnished must be colourless.—Sealed Feb. 17, 1846.

THE CHEMICAL GAZETTE.

No. CIX.—May 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Ozone. By M. Berzelius.

We have frequently had occasion to notice the views and investigations concerning the cause of the smell which is produced in the air and also in oxygen gas by the electric spark evolved on the discharge of the electric battery in water acidified by sulphuric acid, and which Schönbein ascribes to the disengagement of a peculiar substance called ozone, and which, according to his experiments, is likewise formed by a purely chemical process, namely in various slow combustions, especially of phosphorus.

Of late several chemists have experimented upon this interesting body—Schönbein*, Fischer† and Williamson‡. This question may now be regarded as solved by the admirable investigations of Marignac§, from which he concludes that ozone is oxygen gas in a different modification to that in which it occurs in the air and ordinary oxygen gas.

Marignac's experiments have shown—

1. That ozone is obtained in the hydroelectric discharge through water mixed with sulphuric acid, which has been previously freed entirely from nitrogen and oxygen. When the experiment is made *in vacuo*, there is just as much ozone contained in the evolved gas after two hours as at the very first commencement; consequently the presence of nitrogen is not requisite for its production. But no ozone is produced when the liquid is warm.

2. No ozone is generated by boiling peroxide of lead with dilute sulphuric acid; and what is formed in those experiments in which the production of ozone has been considered to have resulted, is a trace of nitrous acid, which reddens moist litmus-paper but does not bleach it.

3. The method which yields ozone quickest and most abundantly consists in passing a current of air slowly through a tube 1 metre long and 6 millimetres internal diameter, containing pieces of phosphorus.

4. Perfectly dry air does not afford any ozone; the phosphorus is coated with an anhydrous combination of phosphorus and oxygen;

* Phil. Mag., xxvii. p. 386. † Poggendorff's Annalen, lxvi. pp. 163–168.
‡ Phil. Mag., xxviii. p. 372. § Ann. de Chim. et de Phys., xiv. p. 252.

and the current of air which escapes only possesses an odour of phosphorus.

5. Air which has been first passed over incandescent copper does not produce any ozone in this manner until the copper is oxidized, when a formation of ozone immediately takes place, even when the air has been deprived of so much oxygen by the copper that a burning taper is extinguished in it.

6. Oxygen gas does not give rise to the production of ozone; it merely acquires an odour of phosphorus.

7. Nitrogen, prepared by boiling nitrite of ammonia, yields ozone when mixed with one-fourth its volume of oxygen just as well as atmospheric air in the experiment previously mentioned.

8. The presence of a trace of nitrous acid prevents the formation of ozone.

9. Carbonic acid yields no ozone; but after being mixed with from one-fourth to one-eighth of oxygen, ozone is formed on passing the mixture over phosphorus, but not to such an extent as with air. When the carbonic acid is removed from the mixture by hydrate of potash, so that only oxygen is left, the formation of ozone ceases entirely.

10. Hydrogen alone does not produce any ozone; but if only a very little oxygen be mixed with it, it induces the formation of ozone to a far greater extent than any other gaseous mixture. The phosphorus fumes strongly, disengages much heat, and is very liable to take fire; so that Marignac considers this mode of production dangerous.

11. Ozonized air, on being passed through a tube heated to between 572° and 752°, absolutely loses every trace of ozone.

12. Ozone does not appear to be absorbed by water, concentrated sulphuric acid, caustic ammonia, barytic water, or chloride of calcium; on the contrary, it is absorbed with the greatest ease by a solution of iodide of potassium, which gradually becomes yellow, iodine being carried away, and the odour of ozone entirely disappears. The solution at last becomes colourless, and then contains only iodate and carbonate of potash, formed by the action of the carbonic acid of the atmosphere.

13. When an ozoniferous atmosphere is passed through a sufficient quantity of moist cotton or asbestos, to remove every trace of phosphorous acid, and then passed over finely-divided silver, for instance as it is obtained on burning the acetate of silver, the odour of the gas disappears, and the silver is converted into a black mass, which after proper drying yields, when heated to redness, not a trace of anything but silver and inodorous oxygen. Ozone is likewise absorbed by other finely-divided metals; but if every trace of water has been removed from the gaseous mixture by desiccation, the ozone does not act upon the metals, not even on zinc, and its odour then persists. When, however, a great portion of the water has been removed, and just a little left, the ozone is absorbed by the silver, which is converted into peroxide of silver, possessing a brown colour, and differing from what has hitherto been considered as peroxide of silver (which is a combination of 4 atoms of peroxide with

1 atom of neutral salt) in this respect, that the free peroxide, on being brought into contact with water, is immediately decomposed into oxygen, which is evolved, and oxide of silver.

From these experiments Marignac has drawn the conclusion that ozone is most probably a peculiar modification of oxygen; but considering the circumstance that it is not produced by absolutely dry gases, he has left it undecided whether it may not perhaps contain some hydrogen.

This last uncertainty, however, has been removed by an experiment of De la Rive. Chlorate of potash is fused to remove all moisture, and then a slow current of dry oxygen disengaged from it; this is passed through a glass tube of about 1 line internal diameter, into which two pieces of platinum wire have been fused, so that they are a small distance from and opposite to each other. Now when a current of electricity is conveyed to the earth through the wires of the conductor of an electrical machine in action, a succession of sparks results between the wires, and the oxygen is thereby converted into ozone, which is recognised by its powerful odour and its reactions, especially towards iodide of potassium and starch, which is most readily observed. As soon as the electric current ceases, unaltered oxygen again issues from the tube.

We have thus arrived at the highly important result, that ozone is no peculiar element, and likewise that it is not an unknown combination of known elements, but that it is oxygen in a different allotropic condition to the ordinary oxygen gas, as this is contained in the atmosphere or obtained in chemical experiments. Our knowledge of the dissimilar allotropic states of the elementary substances * has thus obtained an unexpected and highly remarkable addition. In accordance with the other elements, we may represent it by the symbols $O\alpha$ and $O\beta$. $O\alpha$ is distinguished from $O\beta$ by its odour, and by the tendency it has to form combinations in circumstances under which the latter is perfectly inactive, similar to what likewise occurs with other elements. Whether these modifications are preserved in the combinations or only one of these states, and which belongs to the oxygen in combination, are questions which still remain to be answered. We have seen that the electrical spark converts a certain quantity of $O\beta$ (probably corresponding to the capacity of the spark) into $O\alpha$, and this satisfactorily explains the electric odour. We have, moreover, learned that those bodies which become oxidized at low temperatures, for instance phosphorus, are likewise capable of producing a change; but that in this case the presence of another gas besides oxygen is absolutely requisite, as hydrogen, nitrogen, or carbonic acid; but whether these gases take an active part, or remain passive and merely dilute the oxygen, is not yet known. I may call to mind the effects of phosphorus upon oxygen by mere rarefaction under the air-pump, which have not yet been satisfactorily explained. Is $O\alpha$ likewise formed under these circumstances?

* We may refer the reader to the important observations of Berzelius on this subject in Taylor's 'Scientific Memoirs,' Part XIV.—Ed. *Chem. Gaz.*

There still remains to examine the comprehensive field of extremely interesting comparisons between the different properties of these two allotropic modifications, a subject of inquiry of the greatest importance for science. We have already become acquainted with the mysterious statement of Leuch, according to whom Oα (galvanized air) can be used with considerable advantage for bleaching purposes, and indeed surpasses all other bleaching materials.—Berzelius's *Jahresbericht*, xxvi.

Analysis of the Bile of Boa Anaconda. *By* A. Schlieper.

The bile was first evaporated to dryness, then treated with spirit, which left the greater part of the mucus and the colouring substance undissolved. The spirituous solution was perfectly decolorized by animal charcoal, evaporated at a gentle heat to a thick syrup, and this treated with æther as long as any cholesterine was removed. The residuary bile was now treated with perfectly absolute alcohol, in order to free it from chloride of sodium and sulphates, on which account it was first dried and reduced to fine powder, and mixed in the cold with recently rectified absolute alcohol. The alcoholic solution of pure bile was evaporated in the water-bath, and left a yellow tenacious gummy mass, which on cooling was easily reduced to a fine powder. As long-continued drying at 212° was not sufficient to remove the whole of the hygroscopic water, it was dried at 266°–269°. In this operation the bile cakes together, especially at the beginning, and puffs up, on which account it must be repeatedly rubbed to powder; the desiccation is continued until a carefully weighed quantity no longer loses anything after 4 to 5 hours, when the quantities destined for analyses are immediately weighed off. The carbon and hydrogen were determined with chromate of lead; the nitrogen, according to Dumas's method; the perfectly white ash, obtained by heating to redness for several hours, had an alkaline reaction, and contained neither carbonate of soda nor potash, but consisted almost entirely of sulphate of soda, mixed with very minute traces of chloride of sodium and phosphate of soda. To determine the sulphur, the bile was fused with a mixture of pure nitre and carbonate of soda or caustic potash; upon this it was dissolved in water, supersaturated with hydrochloric acid, and the sulphuric acid precipitated by chloride of barium. The author obtained—

Carbon	58·17	58·09	
Hydrogen.....	8·46	8·57	
Nitrogen	3·41		
Sulphur.....	6·31	6·00	6·38
Ash	11·52		

Liebig's *Annalen*, lx. p. 109.

On some Salts of Arsenic Acid. By M. Setterberg.

Arseniate of Soda.—This salt has the same property as the phosphate of retaining 1 atom of water at 392° F., which is only expelled

at a red heat. The ordinary crystallized salt, which contains 25 atoms of water, effloresces until but 1 atom of water is left in it; but it loses the last atoms very slowly by efflorescence. The salt, on the contrary, which has crystallized above 64°, and contains 16 atoms water, does not effloresce at all at 68° F. If the arseniate of soda be allowed to crystallize at 32°, a salt separates in radiate masses, which contains 27 atoms water.

Arseniate of soda and sulphate of soda form a double salt, which is obtained when the two salts are dissolved in equivalent proportions and crystallized, and also when anhydrous arseniate of soda is heated in a current of dry sulphurous acid, when half the arsenic acid is reduced to arsenious acid and sublimed. The residue, dissolved in water and evaporated, yields first the double salt, and then sulphate of soda. The double salt is $NaOSO^3 + 2NaO, As^2O^5$. It does not effloresce in the air, and melts far more readily than either of the two salts separately.

Arseniate of Baryta, precipitated from a solution of chloride of barium with arseniate of soda, with the precaution that the liquid contain no excess of chloride of barium, is, whether the precipitation be made in the cold or with the application of heat,

$$2BaO, As^2O^5 + 3HO,$$

and contains 9 per cent. water.

When arseniate of baryta is dissolved in arsenic acid, an acid salt separates on evaporating the solution, which contains 8·76 per cent. water, and is $BaOAs^2O^5 + 2HO$. When a large excess of the acid is employed for this solution, and it is evaporated upon the sand-bath nearly to dryness, an insoluble barytic salt is obtained on the addition of water in the form of a white powder, consisting of $BaO, 2As^2O^5 + 4HO$, and which is far less soluble in water than the neutral salt; it is only slightly decomposed by boiling water, while the crystallized $BaOAs^2O^5$ is decomposed by cold water. As this salt cannot be obtained without the application of great heat, the acid appears to exist in it in an analogous state to that of Graham's metaphosphoric acid.

Arseniate of Silver cannot be obtained in the moist way in any other form than as the brown $3AgO, As^2O^5$. But when 1 atom of hydrated arsenic acid is fused with 2 atoms of nitrate of silver until the whole of the nitric acid has been expelled, the neutral salt is obtained in the form of a yellow residue, which is however immediately decomposed by water, the brown basic salt being eliminated. When this is dissolved in nitric acid, and the solution evaporated until nitric acid begins to go off, a basic salt separates on cooling in minute black crystals, and on subsequent gentle evaporation crystals are obtained from the syrupy mother-ley of a double salt of the two acids, which cannot be distinguished in appearance from nitrate of silver; but as soon as they come in contact with pure water, they are decomposed with elimination of the brown basic salt.

When $3AgO, As^2O^5$ is dissolved in free arsenic acid and the solution evaporated, a colourless salt is obtained, which is represented by the formula $AgOAs^2O^5 + 2HO$. This salt is likewise

decomposed by water, and the acid ley deposits the brown basic salt when mixed with water. When concentrated sulphuric acid is poured over the basic silver salt, and the excess expelled at a gentle heat, there is finally left a fused salt, which consists of

$$2AgO, As^2O^5 + AgOSO^3.$$

This latter is not merely decomposed by water, but likewise by sulphuric acid diluted with water, the basic salt being formed.—Berzelius's *Report*, 26th year.

On Palmitonic and Palmitic Acids. By Dr. H. Schwartz.

In order to prepare palmitic acid, discovered by Fremy in palm oil, the author endeavoured to free the commercial acid as much as possible from oleic acid by pressure, and to decolorize it by exposure to the air. Now when the acid was melted, after frequent recrystallization from alcohol, it presented a constant point of solidification at 124° F., and a melting-point of 125°–126°, while palmitic acid melts at 140°. This property remained constant even after the acid had been saponified several times, so that it could not be regarded as identical with palmitic acid; moreover, it did not crystallize from alcohol like palmitic acid in broad laminæ with a satiny lustre, but in dull, dazzling white granular masses; when the solution was more dilute and allowed to cool very slowly, it separated in stellate flakes, which appeared under the microscope to be composed of little laminæ arranged side by side. After solidification upon fusion, it likewise differed decidedly from the laminar crystalline palmitic acid; it was then transparent like wax, the surface of fracture slightly fibrous, and exhibited at several points upon the surface concentric waves, a character which allows of distinguishing this acid even when it contains a large amount of oleic acid; lastly, it could be distilled over unaltered, being merely coloured brown when allowed to flow back frequently along the heated sides of the retort; the melting-point then became lower, and an empyreumatic odour was perceptible. Not a trace of sebacic acid could be extracted from the distillate by boiling water, which proves the total absence of oleic acid. Saponified with potash and dissolved in hot alcohol, it gave on cooling a transparent gelatinous soap, in which dendritic crystals formed after long standing; and at last the entire mass became white and opake. On adding an excess of ammonia to an alcoholic solution of the acid, a faintly crystalline powder containing ammonia subsided, which formed with water a turbid solution, which gave with chloride of barium, nitrate of silver and acetate of lead, white caseous precipitates very sparingly soluble in hot alcohol. The combustion was made in a current of oxygen, the substance being placed in a porcelain boat. The free acid yielded—

Carbon.....	74·422	74·373	74·719	74·693	31	=2325·0	74·669
Hydrogen....	12·368	12·277	12·468	12·354	31	387·5	12·450
Oxygen.....	..	..	..	..	4	400·0	12·881

When the acid was distilled, the first portions, which were very

white, but somewhat opake, and more easily reduced to powder, presented the same melting-point of 124°; but if it had returned often down the sides of the retort, fell to 120°, sometimes even to 115°, and the distillate was yellowish, had a stronger odour, and yielded on analysis a larger amount of carbon; but on purifying the acid by recrystallization from alcohol, the melting-point rose to 123°–124°, and the amount of carbon decreased. The salts of the acid are amorphous, like those of the fatty acids in general, with the exception of the ammonia salt, and not neutral, at least those examined, so that only the amount of carbon and hydrogen of the anhydrous acid can be calculated from them by deducting the base. The baryta salt was prepared by dissolving the ammonia salt in alcohol, and precipitating with an aqueous solution of chloride of barium. The white precipitate which formed was first washed with hot water, then with hot alcohol, in which it dissolved slightly. It yielded on analysis—

	I.	II.	III.	IV.			
Carbon	..	..	60·100	60·593	31	2325·00	58·759
Hydrogen	..	..	9·759	9·881	30	385·00	9·477
Oxygen	..	..	..	..	3	300·00	7·581
Baryta	21·547	21·87	21·344	21·522	1	956·88	24·183

This then would be an acid salt. If we assume, in accordance with analysis IV., the amount of baryta to be 21·5 per cent., we obtain for the anhydrous acid the formula $C^{31} H^{30} O^3$. Another basic baryta salt, obtained by adding an alcoholic solution of the acid to a strongly ammoniacal solution of chloride of barium, gave 26·026 per cent. BaO. The silver salt, prepared in the same manner as the first baryta salt, carefully avoiding any excess of ammonia, which would have dissolved it and turned it brown, gave—

Carbon	..	..	55·648	31	2325	52·247
Hydrogen	..	..	9·503	30	375	8·427
Oxygen	..	..	..	3	300	6·742
Oxide of silver	28·350	28·278	..	1	1450	32·584

The æther of the new acid, which is easily obtained pure, afforded more satisfactory results. To prepare this, some of the purest acid was dissolved in hot absolute alcohol, and dry hydrochloric acid passed into the liquid kept warm by a water-bath; the ætherification was rendered perceptible by a sudden opacity and the gradual separation of oily drops, the new æther being somewhat difficult of solution even in hot alcohol. When it had been sufficiently freed from muriatic acid and alcohol by washing with hot water, it solidified at 77° F. to a distinctly crystalline mass, which remained constant even after distillation, and at the same time afforded a further proof of the absence of oleic acid. The æther crystallized from alcohol on cooling in soft, broad, shining plates, which reflected the light almost like chlorate of potash; but owing to their low melting-point they easily deliquesce on the filter. Analysis yielded—

Carbon	75·671	75·958	75·991	75·755	35	2625	75·812
Hydrogen	12·469	12·525	12·692	12·621	35	437	12·635
Oxygen	..	..	..	..	4	400	11·553

The æther prepared from the distilled acid presented, like the latter, an excess of carbon, viz. 76·195 per cent.

When the acid was heated in a flask with crude nitric acid of 1·200 spec. grav., a moderate evolution of nitrous acid resulted; and after boiling for some length of time, it became more and more yellow, softer, and at last oily. The acid obtained from three portions, removed after 2, 6 and 12 hours' action, and recrystallized from alcohol, exhibited a constant point of solidification at 124°, the dull granular separation from alcohol, the concentrically waved surface after solidification, and the same composition as the new acid.

The oily body which Bromeis obtained from stearic and elaic acids, and which yields a red soap with potash, is also formed, even from the purest acid, by the action of nitric acid.

To ascertain the difference between the above acid and palmitic acid, the author attempted to prepare it from the crude expressed palm oil. This was saponified with potash, dissolved in hot alcohol, and allowed to cool; instead of the transparent gelatinous soap, a beautiful crop of crystals, in concentric, radiate, warty patches, was now obtained. After frequent recrystallization of the potash salt, decolorization with animal charcoal, decomposition with muriatic acid, and recrystallization of the acid from alcohol, the author finally obtained an acid which melted at 140°, solidified at 136°, separated from alcohol in broad satiny laminæ, and when fused solidified to a very crystalline mass. The analyses agreed with those of Fremy and Stenhouse, viz.—

Carbon	74·929	74·991	74·870	74·819	32	=2400	75·0
Hydrogen ..	12·491	12·468	12·461	12·549	32	400	12·5
Oxygen	..	..	..	..	4	400	12·5

This palmitic acid cannot be distilled wholly unaltered even in an atmosphere of carbonic acid; it remains tolerably colourless, but the point of solidification sinks to 135°. By recrystallization from alcohol, however, pure palmitic acid is again obtained. The æther compound was obtained in the same manner as that of the new acid, and exhibited perfectly similar properties, with the exception of solidifying at 70°. It yielded on analysis—

Carbon	75·449	75·590	75·309	68	=5100	75·407
Hydrogen.....	12·717	12·740	12·530	68	850	12·592
Oxygen	..	..	..	8	800	12·001

The rational formula, according to Stenhouse, is

$$C^{32}H^{31}O^{3}, HO + C^{32}H^{31}O^{3} + AeO;$$

or, more probably, according to Fremy, $C^{64}H^{62}O^{6} + HO, AeO$.

The author failed in preparing palmitine from the crude expressed palm oil, as it could not be freed, even by boiling with alcohol for eight days, from a red oily substance, which is somewhat difficult of solution in hot alcohol. Nor could the two substances be separated by the gradual addition of alcohol to the æthereal solution. On exposure to the air, it was decolorized even in the cold. To determine

the atomic weight of the palmitate of potash, it was dried at 212°, when it melted to a transparent mass. It was reduced to ash. The carbonate of potash, fused over a spirit-lamp and quickly weighed after cooling over sulphuric acid, gave 8·291–8·316 per cent. KO, which numbers accurately correspond with theory.

On exposing palmitic acid between 482° and 572° to the air for some time, it passed, with formation of water and carbonic acid, into the new acid, which the author proposes to name palmitonic acid.—Liebig's *Annalen*, lx. p. 58.

On Sulphoxyphosphovinic Acid and its Compounds. By M. Cloez.

In a previous communication I described, conjointly with M. Bouquet, a new class of salts, whose acid, which we named sulphoxyarsenic acid, contains arsenic, oxygen and sulphur at the same time, as well as water. The sulphoxyarseniate of potash, which we obtained by passing sulphuretted hydrogen through a solution of arseniate of potash, is represented by the formula $AsO^3 S^2, KO + 2HO$.

The great analogy which exists between the corresponding compounds of arsenic and phosphorus led us to suspect the existence of sulphoxyphosphates. After numerous experiments I succeeded in producing these salts by decomposing the chlorosulphuret of phosphorus of M. Serullas with a solution of caustic potash. The chlorosulphuret of phosphorus, treated with ordinary alcohol, yields an acid analogous to the phosphovinic acid of M. Pelouze. According to my analysis its formula is $PhO^3 S^2, C^4 H^5 O, 2(HO)$; it is sulphoxyphosphovinic acid. Wood-spirit gives sulphoxyphosphomethylic acid. Amylic alcohol should produce the corresponding sulphoxyphosphamylic acid.

On saturating the sulphoxyphosphovinic acid with carbonate of baryta, lime, strontia, &c., definite crystalline salts are obtained; the baryta salt is $PhO^3 S^2 C^4 H^6 O, 2BaO + Aq$. The salts of potash and soda are readily obtained by decomposing the chlorosulphuret of phosphorus with an alcoholic solution of potash or soda; they are soluble in alcohol. The following equation exhibits the reaction which takes place with potash:—

$$PhCl^3 S^2 + C^4 H^6 O^2 + 5(KO) = PhO^3 S^2, C^4 H^5 O\, 2(KO) + 3(KCl) + HO.$$

Comptes Rendus, March 8, 1847.

On the Action of Charcoal on Metallic Salts and some Vegetable Substances. By F. Weppen.

It is well known that charcoal has the property of combining with various metallic salts and vegetable substances, besides colouring matters; it was important, therefore, to ascertain whether charcoal which has served to precipitate one metal, and is as it were saturated with it, would still be capable of precipitating another, although a different order were followed to that in which one metal is precipi-

tated by another. For this purpose, 200 grs. of charcoal, which had been employed to precipitate corrosive sublimate, were shaken with a solution of 5 grs. of sulphate of copper in 2½ oz. of water. The reaction with sulphuretted hydrogen for copper soon became very slight, most of the copper had been precipitated, and the remainder was precipitated on adding a few drops of caustic ammonia to the liquid. The charcoal was washed, dried and shaken with a solution of 3 grs. of protosulphate of iron. When after some time there was no longer any reaction with ferridcyanide of potassium, 2 grs. more of the protosulphate were added. It was found that the carbon could decompose 11 grs. of the salt.

It was to be expected that the precipitation of the metals would result more rapidly if the above order (mercury, copper, iron) was reversed. Such was found to be the case. Charcoal, which had been employed in the last experiment to precipitate the sulphate of iron, threw down from a solution of 4 grs. of sulphate of copper, which were gradually added, the whole of the copper with the exception of a slight trace much quicker, and the subsequently-washed charcoal acted powerfully on the solution of corrosive sublimate, although it was quite saturated with mercury at the very beginning of the experiment. This charcoal containing mercury had a remarkable action upon sulphate of iron, of which it again threw down nearly 3 grs. To ascertain whether, in case any double decomposition ensued in the charcoal, the new salt produced existed in solution, 40 grs. of animal charcoal were left for several days in contact with 10 grs. of protosulphate of iron, then filtered, washed, dried, and shaken with a solution of 10 grs. of chloride of barium. No iron passed into the solution in the cold, but on boiling, the liquid yielded a slight reaction with ferridcyanide of potassium. Since, through the medium of charcoal, sulphuretted hydrogen and oxygen decompose each other in such a manner that sulphur is eliminated in the charcoal, it was to be expected it would likewise favour other reactions; but no baryta could be precipitated from a solution of chloride of barium by charcoal saturated with carbonic acid; nor could salts of zinc or iron be precipitated with charcoal saturated with sulphuretted hydrogen. Nitrate of silver could not be decomposed by hydrogen when the latter was passed into a solution of the former in which animal charcoal was suspended, although silver reduced by hydrogen in the circle of the galvanic battery is said to be precipitated on the charcoal serving as anode.

In another series of experiments, 2 oz. of animal charcoal were digested with a solution of 6 drms. of extract of wormwood mixed in distilled water. As soon as the liquid had lost its bitterness, it was filtered and evaporated; a brownish mass, which had an acid taste and reaction, was obtained, from which, by rinsing with water, some distinct crystals were separated. Chlorine, sulphuric acid and potash could readily be detected in it; moreover, the solution yielded, when saturated with caustic ammonia and boiled to expel the excess, a precipitate with a neutral solution of perchloride of iron, indicating the presence of succinic acid, which according to Zwenger occurs in

wormwood as an acid potash salt; consequently charcoal affords an excellent means of detecting certain vegetable salts in the extracts of plants. The solutions of the bitter extracts or tinctures are generally decolorized previously to losing their bitterness; this induced the author to ascertain whether the bitter principle of wormwood could not be obtained pure and colourless by means of charcoal from a concentrated tincture of wormwood. When the beautiful green-coloured tincture, prepared from 6 oz. of wormwood with 24 oz. of alcohol, had been decolorized with ivory-black, the bitter liquid was filtered, and the greater portion of the alcohol removed by distillation. On further evaporation, a brownish oleo-resinous substance separated from it, in which some crystals were perceptible; the latter could be extracted with water; they consisted of chloride of potassium, with a little sulphate of potash. The residuary brown resinous substance was now again dissolved in some alcohol, to which it imparted an intense bitter taste, and was left to spontaneous evaporation. At first some white flakes separated from the brown liquid; but as the evaporation proceeded, the brown resin again made its appearance. When the charcoal which had been employed to decolorize the green tincture was boiled with alcohol, this was very little coloured by it, but became intensely bitter, proving that the bitter principle is precipitated at the same time with the colouring principle. On evaporating the alcohol, a small quantity of nearly white flakes, which are extremely bitter, are obtained.

Scarcely anything can be extracted from the charcoal which has been employed to precipitate extract of gentian by boiling with alcohol and æther; but if it be treated with a solution of carbonate of soda, the solution acquires a beautiful yellow colour; and on evaporation, treatment with dilute sulphuric acid, and then with alcohol, yields a precipitate of sulphate of soda, and a golden tincture which has not the least bitter taste, and from which on slow evaporation no crystals of gentianine were obtained.—Liebig's *Annalen*, p. 354.

On the Composition of Theobromine and some of its Combinations. *By* K. E. Glasson.

The researches of Mulder and Jobst have established the identity of caffeine and theine; the latter, moreover, showed that guaranine has exactly the same composition as caffeine. This remarkable occurrence of caffeine in three families of plants so widely distinct led Woskresenski to the discovery of a peculiar principle in cacao berries, which he called theobromine. It is obtained from the berries as they occur in commerce, by extracting them with boiling water, and straining the extract through linen. A solution of acetate of lead produces a large precipitate, which is separated by filtration, and the liquid, freed from an excess of lead, is evaporated to dryness. The residue, which still contains colouring matters, is treated with boiling alcohol, from which on cooling the theobromine separates as a white, faintly-reddish crystalline powder; it is obtained perfectly pure by frequent recrystallization. It has a slightly bitter

taste, which from the sparing solubility of the substance is slowly perceived; and is not altered by exposure to the air nor at 212°. At 482° it becomes brown, and is volatilized at a higher temperature, leaving a residue of carbon, and forming a crystalline sublimate. It is sparingly soluble in hot water, still less so in alcohol and æther. It dissolves readily when boiled with barytic water, apparently without decomposition; there was no evolution of ammonia, but on cooling the solution formed a white jelly.

Pure theobromine, precipitated by dilute ammonia from the crystallized muriate, well-washed, and dried at 212°, yielded on analysis—

	I.	II.	Woskresensky.				
Carbon.....	47·13	47·13	47·21	46·97	14	=1050	46·67
Hydrogen	4·60	..	4·53	4·61	8	100	4·44
Nitrogen	31·23	31·32	35·38	..	4	700	31·11
Oxygen	17·04	..	..	..	4	400	17·78

The numbers for the carbon and hydrogen agree perfectly with those found by Woskresensky, but the amount of nitrogen obtained by him is too high.

Theobromine and Muriatic Acid.—Theobromine dissolves readily in concentrated muriatic acid, and on cooling a salt separates which is decomposed by water, a basic combination being eliminated; it loses the whole of its muriatic acid at 212°, and yields on analysis 16·17 per cent. chlorine, which corresponds to $C^{14} H^8 N^4 O^4$, HCl.

Theobromine and Nitric Acid.—When theobromine is dissolved at a gentle heat in nitric acid, and the clear acid solution set aside to cool, this salt crystallizes after some time in oblique rhombic prisms; like the muriate, it is readily decomposed by water, and parts with the whole of the nitric acid at 212°. It gave on analysis 22·87 per cent. nitric acid, corresponding to $C^{14} H^8 N^4 O^4 + NO^5$, HO, which requires 22·22 per cent.

Theobromine and Nitrate of Silver.—If nitrate of silver be added to a very dilute solution of nitrate of theobromine, this salt soon separates in silvery white shining needles. It is remarkable from its extreme insolubility, and may serve as an excellent test for theobromine. There is scarcely any loss at 212°; but if the temperature be increased, it melts, giving off red vapours of nitrous acid. When heated to redness for some time with access of air, the silver left exhibits a metallic lustre, and dissolves entirely in nitric acid. It gave on analysis—

Carbon.....	23·71	23·71	..	14	=1050	24·00
Hydrogen.....	2·47	..	..	8	100	2·28
Nitrogen	..	19·76	..	5	875	20·00
Oxygen.....	..	..	..	9	900	20·58
Oxide of silver.....	32·67	..	33·02	1	1450	33·14

leading to the formula $C^{14} H^8 N^4 O^4 + AgONO^5$.

Theobromine and Chloride of Platinum.—When chloride of platinum is added to a muriatic solution of theobromine, this combination separates in beautiful monoklinometric prisms, which effloresce

by long exposure to the air, and lose the whole of their water of crystallization at 212°; at a higher temperature it is decomposed; and on ignition with access of air, the platinum is left of a silvery-white colour. Its composition is represented by the formula $C^{14}H^8N^4O^4$, $HCl + PtCl^2$, 4Aq.

The atomic weight of theobromine being thus established, we find on comparison a very simple relation to exist between it and caffeine:—

1 equiv. caffeine = $C^{16}H^{10}N^4O^4$ Stenhouse.
1 equiv. theobromine = $C^{14}H^8N^4O^4$
C^2H^2

Caffeine differs therefore from theobromine by containing an additional C^2H^2.

Decomposition of Theobromine with Peroxide of Lead and Sulphuric Acid.—When a mixture of theobromine, peroxide of lead and sulphuric acid is heated in a retort, evolution of carbonic acid results; and the decomposition once begun, proceeds without any further application of heat. It is necessary to be extremely cautious with the addition of the peroxide of lead, as the object is to effect an imperfect oxidation; but when an excess of peroxide is used, or the mixture is heated too strongly or too long, the newly-formed body is entirely decomposed, and none of the following phænomena can be observed. When the reaction is complete, the liquid filtered from the sulphate of lead is clear, colourless and faintly acid; it disengages ammonia with caustic potash, and on mixing it with sulphuretted hydrogen, *sulphur* is eliminated; it colours the skin purple; mixed with calcined magnesia, it is instantly coloured *indigo-blue*; an excess of magnesia destroys the blue colour, but it can be restored by the cautious addition of sulphuric acid. If the liquid, to which an excess of magnesia has been added, is evaporated to dryness on the water-bath, ammonia is evolved, and the mass becomes slightly red; this body may readily be extracted with boiling alcohol, from which it separates on cooling in colourless, faintly-acid rhombic prisms. The crystals are readily soluble in alcohol, and do not enter into combination either with chloride of platinum, nitrate of silver, or the perchloride of mercury. I have not been able to examine this body more minutely, from want of material; but its behaviour towards sulphuretted hydrogen, and imparting a purple colour to the skin, points to a similarity to alloxan.—Liebig's *Annalen* for March, p. 335.

On a Mode of removing Nitrate of Silver Stains from Linen.
By William Bird Herapath.

Medical men, in the habit of using the nitrate of silver extensively as a remedial agent, must have frequently heard loud complaints of their patients' linen having been indelibly stained and spoiled, by some accident having occurred during its use; and in many cases patients have refused to employ these preparations in

consequence of the awful destruction of linen which they occasion. I have therefore very little doubt that the following observations will prove most acceptable to the numerous readers of your widely-circulated Journal:—

These dark stains consist of finely-divided *metallic silver* in intimate union with the tissue of the cloth; had they been oxide of silver, any diluted acid would have dissolved them; but nitric acid alone produces any effect, which of course cannot be employed from its powerfully-destructive effects upon the linen fabric.

Iodine immediately converts them into iodide of silver, which is instantly dissolved by a solution of hyposulphite of soda, and the cloth remains as white as when first issued from the bleaching-house, and as firm and durable as ever. The best mode of employing this substance is to strain the spotted linen over a basin of hot water, and then to let fall a few drops of tincture of iodine upon each spot previously moistened with water; then instantly to pour sufficient of the solution of the hyposulphite of soda to dissolve the iodide produced, and immediately to immerse the spot in the water beneath; and to wash out and cleanse the tissue at once from the stain and the chemical reagents employed. The tincture of iodine of the London Pharmacopœia is the strength I use; and 1 drm. of hyposulphite of soda dissolved in 2 oz. of water will make an excellent bleaching liquid.—*Pharmaceutical Journal*, April 1847.

Upon the Action of Chlorine on Urea, and a new Method of preparing Cyanuric Acid. By Dr. J. E. de Vry.

When muriate of urea, obtained by passing dry muriatic acid over powdered urea, is heated in an oil-bath, it is violently decomposed at 293°, with disengagement of chloride of ammonium, while the temperature rises above 392°, although the bath was immediately removed. On dissolving the solid mass in hot water, a large quantity of snow-white cyanuric acid is obtained on cooling, and the mother-ley contains chloride of ammonium.

When, instead of removing the bath at 293°, the temperature is raised to about 608° and the mass heated with water, cyanuric acid is no longer obtained, but the white body discovered by Liebig and Wöhler.—Liebig's *Annalen*, Feb. 1847.

Analysis of Bat's Dung. By T. J. Herapath.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—I noticed an account, a few weeks ago, in one of the scientific periodicals, of a discovery of the utility of bat's dung as a manure, by an Englishman resident in the West Indies: I beg leave to say, that in 1844 Mr. Cowell of Bristol sent a substance to my father for analysis, which he said was bat's dung, and was found in considerable quantity in a cave on his estates at Jamaica. He had noticed the great crops produced on land manured with guano, and

conceived that this substance could be substituted for it with the same good effects.

Upon analysis, my father found it to contain in the 100 parts—

Water and organic matter	84·4
Soluble salts, consisting of phosphate of potash, sulphate of soda, sulphate of magnesia, and chloride of sodium	4·5
Phosphate of lime	9·9
Earthy residue	1·2
	100·0

5 grs., treated by Varrentrapp and Will's method, gave ammonio-chloride of platinum, 6·568 grs., which is equal to nitrogen, 0·417 gr.

Therefore it contains of nitrogen 8·34 grs. per cent., which is equivalent to ammonia, 10·127 grs.

It therefore appears that, with the addition of from 10 to 14 per cent. of phosphate of lime, it would be equal in fertilizing power to the best Ichaboe guano.

The dung formed a stratum on the floor of the cave of 2 or 3 feet in thickness, of a dark fawn colour.

This stratum was composed of the excrements of various species of bats, principally belonging (as near as I could ascertain by the description) to the class Pteropina, of the second division Anistiophori, which had probably collected there for centuries.

I remain, Sir,

Old Park, Bristol,
March 30, 1847.

Yours respectfully,
Thomson J. Herapath.

ANALYTICAL CHEMISTRY.

On a quick Method of determining the Amount of Nitrogen contained in Organic Substances. By E. Peligot.

The knowledge of the amount of nitrogen contained in organic substances has become of such importance for the study of questions relating to physiology and agriculture, that a quicker and more simple method of determining this element than those in use will undoubtedly prove acceptable.

The ordinary process, which consists in collecting the nitrogen in the state of gas, requires several hours, and is extremely fatiguing, especially in such cases where the nitrogen determinations require to be numerous, as is the case in most of the researches in physiological and agricultural chemistry; the method proposed by MM. Will and Varrentrapp likewise presents many serious inconveniences. The combustion of the organic substance in the presence of soda-lime is quicker than by the preceding process; but the estimation of the ammonia which it yields is very tedious, on account of the evapora-

tion of the platinum salt on the water-bath, its filtration, washing and drying at a fixed temperature. Moreover, the weight of the salt is frequently rendered uncertain, owing to the presence of liquid hydrocarbons, which the æther and alcohol remove with great difficulty. Moreover, it is known how rapidly a pulverulent compound, like the ammonio-chloride of platinum, absorbs a greater or less quantity of moisture from the air.

The process which I propose is a very simple modification of MM. Will and Varrentrapp's method; the combustion is executed in the same manner, and the ammonia condensed in a similar bulb-apparatus, but which, instead of containing hydrochloric acid, contains a fixed volume or weight of sulphuric acid of known strength. Now as the ammonia which combines with the acid lowers its strength, by determining after the combustion the composition of this liquid and comparing it with that it previously possessed, it is easy to ascertain the quantity of ammonia it has condensed, and consequently the amount of nitrogen yielded by the substance submitted to analysis.

This operation is executed with as much rapidity as precision by means of an alkaline solution likewise of known strength; I prefer a solution of lime in syrup. It is known that, by triturating slaked lime with a solution of sugar, it dissolves in far greater proportion than in pure water; the compound which forms presents the same alkaline reaction as if the base which it contains were free; it is easily preserved without alteration in bottles protected from contact with the carbonic acid of the atmosphere, as with this acid it forms carbonate of lime; but as this insoluble salt renders the liquid turbid, it need only be filtered to serve again to determine the strength of the sulphuric acid.

I introduce into the condensing apparatus 10 cub. centim. of sulphuric acid of known strength, accurately measured in a narrow graduated pipette; the acid which I employ contains 61·250 grms. of SO^3HO to 1 litre of water; consequently 100 cub. centim. of this liquid correspond to 2·12 grms. of ammonia, or 1·75 grm. of nitrogen.

When the combustion is finished, the acid which has served to condense the ammonia is poured into a cylindrical glass, the apparatus carefully washed, and to this liquid, diluted with much water, a few drops of litmus are added to give it a red colour. By means of the solution of lime in sugar, which is contained in a burette graduated in cubic centimetres and in tenths of a cubic centimetre, the acid liquid is accurately saturated, being guided by the blue colour which the liquid suddenly acquires when the point of saturation is attained. The quantity of alkaline liquid required to produce this effect is read off on the burette; and as the amount of the lime compound which saturates 10 cub. centim. of the normal solution of sulphuric acid has been determined by a previous experiment, by subtracting from this quantity that found for the acid which has absorbed the ammonia from the nitrogenous substance, we find the volume of the acid solution which has been saturated by the am-

monia, and consequently the weight of the nitrogen which the body contained.

I will mention as an example of the use of this method, the accuracy of which I have confirmed on several nitrogenous substances, the determination of the nitrogen in oxamide.

0·417 grm. substance was burnt.

10 cub. centim. of the standard solution of sulphuric acid saturate 33·5 divisions of the burette, containing the alkaline solution of lime in sugar.

10 cub. centim. of the same acid after the combustion saturated 8·5 divisions of the same alkaline solution.

By subtracting 8·5 divisions from the 33·5, we have 25 divisions for the alkaline liquid, representing the quantity of acid saturated by the ammonia given off by the substance analysed; this last quantity is found by rule of three to be 7·46 cub. centim.; now as 10 cub. centim. of the standard acid correspond to 0·175 grm. of nitrogen, 7·46 correspond to 0·130 grm. of nitrogen contained in 0·417 oxamide. We find consequently that 100 parts of this substance contain 31·3 nitrogen; theory requires 31·7.

By proceeding as above directed, a nitrogen determination may be executed in less than half an hour with as much accuracy as by the other methods, which require at least 3 hours.

I have ascertained that substances containing but very little nitrogen, as wheat, vegetable soil, &c. may equally be analysed in this manner, provided a sufficient quantity of the substances be employed. I believe that this process will prove very useful to chemists, especially to those engaged in investigations bearing upon animal and vegetable physiology, by enabling them to multiply, at a far less expense of time and money, determinations which are only of value in as far as they are comparative, and consequently very numerous. —*Comptes Rendus*, March 29, 1847.

On the Employment of the Chloride of Gold for estimating the Presence of an Organic Substance in Solution in ordinary Waters. *By* A. Dupasquier.

The waters of rivers, springs, and especially those from wells and cisterns, all contain a larger or smaller proportion of organic matter in solution. When its quantity is very minute, which is most generally the case, its presence is of no importance either in a sanitary point of view or with respect to its application to the arts; and in this case the presence of this minute quantity is incapable of being detected by any test; it is only found on making a quantitative analysis of the water.

Some waters however are frequently charged to an abnormal extent with organic substances, and their use may prove injurious to the health or unfit for industrial purposes. It is therefore of importance to be able to detect by a simple and ready test the presence of this more than ordinary proportion of organic matter; the nitrate of silver does not answer, and evaporating to dryness and calcination

of the residue is very tedious, and the result moreover very unsatisfactory.

I was led to try the chloride of gold, from it being observed by persons engaged in photography, that this salt is decomposed when added to the condensed water of certain steam-engines, or any other distilled water containing organic matter in solution; I found it answer extremely well. My plan is to take from 25 to 50 grms. of the water to be examined in a small flask; add to it a few drops of a solution of chloride of gold, so as to impart to it a faint yellowish tint, and then boil the liquid. If the water only contains the usual quantity of organic matter, it retains its yellowish tint; if, on the contrary, it contains an abnormal quantity, the water at first becomes brown, and then assumes a bluish tint, which indicates the decomposition of the gold salt; this tint becomes more and more marked by continuing the boiling, if the proportion of organic matter is considerable; but the least brownish tint of the liquid indicates with certainty that the organic matter exceeds the ordinary proportion.—*Comptes Rendus*, April 5, 1847.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

Feb. 15, 1847. (Lieut.-Col. P. Yorke in the Chair.)

Mr. Scanlan announced that he had found iodide of cyanogen in commercial iodine, to the extent of 100 grs. to the pound.

"On the Composition of Caffeine, and of some of its Compounds," by Mr. E. C. Nicholson.

From the numerous experiments on this subject, the composition of caffeine might have been considered as perfectly established. But in a recent investigation on caffeine, M. Payen states that he has obtained numbers which sensibly differ from the results of his predecessors, and which he translates into the formula $C^{16}H^{10}N^4O^3$, which contains 1 equiv. of oxygen less than the investigations up to the present time admitted. For this reason, the author took up the subject, so as to prove the true composition of caffeine. The experiments were made partly with some beautiful caffeine obtained from the laboratory of M. Merck of Darmstadt, and partly with some the author had prepared himself. It was crystallized three times from dilute alcohol, in order to ensure perfect purity, and finally dried in the water-bath at 212° F. Several combinations of the substance led to the formula $C^{16}H^{10}N^4O^4$.

The compound of caffeine and bichloride of platinum is obtained when a solution of caffeine in hydrochloric acid is added to a solution of bichloride of platinum. A beautiful orange-yellow crystalline precipitate falls, which, when washed with alcohol, and dried at 212° F., is perfectly pure. The analyses led to the formula given by Dr. Stenhouse, $C^{16}H^{10}N^4O^4\,HCl\,PtCl^2$.

The singular compound of caffeine and nitrate of silver is obtained when an excess of nitrate of silver is added to a solution of caffeine; it falls down in hemispherical nodules, perfectly white, which require to be washed with water and crystallized from alcohol in order to render them pure. It is not altered when exposed to light, and undergoes no change if boiled with water for a considerable time. The formula deduced from the analysis is $C^{16} H^{10} N^4 O^4$, AgO, NO^5. The only analogues to this compound at present known are, urea and nitrate of silver,

$C^2 H^4 N^2 O^2$, AgO, NO^5, and $C^2 H^4 N^2 O^2$, 2(AgO, NO^5);

glycocol and nitrate of silver, $C^4 H^4 NO^3$, AgO, NO^5; and, according to the experiments of H. Rose, nitrate of silver absorbs 3 equivs. of ammonia.

The compound of caffeine and chloride of mercury is formed when chloride of mercury is added in excess to an aqueous solution of caffeine. The liquid soon becomes filled with a mass of beautiful needle-like crystals, which are very similar in appearance to caffeine; they are soluble in alcohol and water, and may be boiled in the latter without undergoing decomposition. An analysis of this compound led to the formula $C^{16} H^{10} N^4 O^4$, 2(HgCl).

The compound of caffeine and chloride of gold is precipitated when terchloride of gold is added to caffeine dissolved in hydrochloric acid, as a beautiful lemon-yellow powder, which when washed with water is quite pure. It may be crystallized from alcohol, but is decomposed by boiling water. Analysis led to the formula

$C^{16} H^{10} N^4 O^4$, HCl, $AuCl^3$.

March 15, 1847. (The President, Prof. Graham, in the Chair.)

A letter was read from Mr. Coathupe, "On a Method of increasing the Power of Gun-Cotton, by soaking it in a Solution of Chlorate of Potash."

"On the Decomposition of Water by Platinum and Black Oxide of Iron," by Dr. G. Wilson.

The interesting researches of Mr. Grove on the decomposition of water by white-hot platinum, lately made public, have necessarily led to many conjectures concerning the cause of a phænomenon so extraordinary and unexpected. Certain remarkable peculiarities possessed by platinum, and in a less degree by others of the noble metals, have thrown some doubt on the powers of mere heat to effect the decomposition of a compound of such stability as water. The repetition of the experiments with other substances not open to the same objections is, however, a matter of great difficulty. While reflecting on the means of accomplishing this, the attention of the author was accidentally called to the evolution of small bubbles of gas from the fused globules of oxide of iron, produced by burning iron wire in oxygen gas, falling into water. In the hope that this might afford some clue to the phænomenon in question, arrangements were made for performing the experiment in such a manner that the gas evolved should be collected and preserved for examination. This was easily done by directing the fused globules of oxide,

by means of an inclined plane of tin-plate, from the jar in which the wire was burned, under the edge of an inverted funnel entering a test-tube immersed in the water of the pneumatic trough. The quantities of gas disengaged by the globules were very unequal; some gave none at all. Generally, globules from the thickest wire produced most gas. The gas on examination, however, was discovered to be pure hydrogen, merely sullied by a trace of atmospheric air; and its origin was at once explained by an examination of the globules themselves, for very many of these latter were found to contain in their centre a kernel of fused metallic iron, which had escaped oxidation when the wire was burned in the gas, and which in a highly heated state coming in contact with water, occasioned the decomposition of a portion of the latter in the usual manner. The black oxide of iron does not appear to have the power of further extracting the oxygen from water. This experiment is therefore valueless in elucidating the fact of the decomposition of water by heated platinum. It is probable too that the temperature of the melted globules of oxide of iron is really much inferior to that of platinum in the state in which it is employed in Grove's experiment, namely, just at the point of fusion.

Dr. Wilson then argues, that the decomposition of water by a white heat may be referable to the mechanical disruption of the particles in direct contact with the heating body, and not to the decomposing power of heat alone; as the statement that water can be produced by the same processes that disunite its elements would be tantamount to affirming that unlike effects may flow from the same cause, without any alteration in the qualities or conditions of the water.

"On the Preparation of Hippuric Acid," by Dr. W. Gregory.

This is a modification of the ordinary method followed for the preparation of hippuric acid from the urine of the cow, which consists in evaporating at a moderate temperature, to about one-eighth its bulk, adding hydrochloric acid, and boiling the impure crystals of hippuric acid which deposit with milk of lime in excess, as proposed by Schwarz, the excess of lime being separated by filtration, and hydrochloric acid added to the clear solution. In this way colourless hippuric acid is obtained in crystals; but it is found in practice, that a great part of the acid is liable to become converted into benzoic acid, from the fluctuations of temperature during the evaporation. It was evident, from the above process of purification, that the hippuric acid was not decomposed by boiling with an excess of lime; and Dr. Gregory has therefore prevented this loss of the acid by adding milk of lime to the urine before evaporation, separating the excess, and then boiling rapidly down until of the required bulk, and adding hydrochloric acid: the purification is conducted as above, by re-solution in lime, and separation by acid.

THE CHEMICAL GAZETTE.

No. CX.—May 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Glycocoll (Sugar of Gelatine), and some of its Products of Decomposition. By E. N. Horsford.

Sugar of gelatine, which was obtained by Braconnot by treating isinglass with sulphuric acid, has been examined principally by Boussingault and Mulder; according to the latter, it possesses the formula $C^8 H^7 N^2 O^7$, or rather $C^8 H^7 N^2 O^5 + 2HO$. Boussingault, after having advanced several other formulæ for the sugar of gelatine, recently proposed the formula $C^{16} H^{15} N^4 O^{11} + 3HO$, in which 3 equivs. water can be replaced by 4 equivs. of a metallic oxide. For the nitrate of glycocoll he deduces the formula

$$C^{16} H^{15} N^4 O^{11} 4NO^5 + 9HO,$$

and for its combination with bases

$$C^{16} H^{15} N^4 O^{11} + 4NO^5 + 4(8)MO + 2HO.$$

On repeating the examination of glycocoll, the author did not find, on burning it, so large an amount of carbon as Mulder and Boussingault obtained; his researches, on the contrary, lead to the formula $C^4 H^4 NO^3$*. Boussingault's analyses of different compounds of glycocoll agree perfectly well when calculated according to the author's formula, some indeed even better than according to Boussingault's. The author's formula is moreover supported by numerous analyses; by its combinations with sulphuric acid, $C^4 H^4 NO^3, SO^3$; with oxide of copper, $C^4 H^4 NO^3, CuO, HO$, and with nitrate of silver; by its behaviour towards sulphuric acid and a galvanic battery; and lastly, by the composition of hippuric acid.

The author obtained the material for his investigation from hippuric acid, which, as discovered by Dessaignes†, is decomposed on boiling with a strong acid into benzoic acid and sugar of gelatine or glycocoll, to which latter name the author gives the preference. From 3 to 4 oz. of hippuric acid are mixed in a flask capable of holding a quart, with 4 times its weight of concentrated muriatic acid, and

* In his recent investigation (Chem. Gaz., vol. v. p. 3) Mulder arrived at the formula $C^8 H^{10} N^2 O^8$, or $C^8 H^8 N^2 O^6 + 2HO$, which is consequently identical with that proposed by the author.

† Chem. Gaz., vol. iv. p. 14.

heated over a spirit-lamp until entirely dissolved; it is then gradually heated, adding some water about half an hour after perfect solution. A portion of the benzoic acid then separates in oily drops upon the bottom of the vessel, which on the cooling of the liquid solidify to a mass of silky crystals, whilst the muriate of glycocoll remains dissolved in the water. When the greater portion of the benzoic acid has separated, it is collected on a filter, and washed as long as the liquid that passes has an acid taste. This liquid is now evaporated nearly to dryness in the water-bath, when the greater portion of the muriatic and benzoic acids is driven off; by adding more water, evaporating, and repeating this operation two or three times, the muriate of glycocoll is left perfectly pure. Ammonia is now added until the liquid has an alkaline reaction, when a white crystalline precipitate of glycocoll is obtained upon the addition of absolute alcohol, while muriate of ammonia and traces of benzoic acid remain in solution. As glycocoll is but slightly soluble in absolute alcohol, but far more so when the latter contains muriate of ammonia, it is advisable to set the liquor aside for some time. The precipitate is collected on a filter, and washed with absolute alcohol as long as anything is precipitated from the filtered solution by nitrate of silver. The hydrate of glycocoll thus obtained has a sweet taste, but less intense than cane-sugar; it is void of smell, and has no action upon test-paper; dissolves in 4·24 to 4·35 parts cold water; more readily in hot than in cold spirit; it is almost wholly insoluble in æther, and also in absolute alcohol. When heated with a concentrated solution of potash, the liquid assumes a splendid fiery red colour, with evolution of ammonia; the former however disappears on the continued application of heat. The same beautiful colour is apparent when it is heated with hydrate of baryta or oxide of lead. A very small quantity of glycocoll mixed with a solution of sulphate of copper prevents the precipitation of the oxide by potash, and the liquid assumes the characteristic blue colour. If a solution of glycocoll is boiled with oxide of copper, it dissolves it, the liquid assuming a blue colour, and on cooling a substance crystallizes from it in fine needles. With protonitrate of mercury a precipitate is obtained of metallic mercury. From a concentrated solution in dilute alcohol or water, crystals are obtained on spontaneous evaporation, which belong to the monoclinometric system. The analyses of this body made with chromate of lead gave—

Carbon	31·89	32·31	31·81	..	..	4=24		32·00
Hydrogen ..	6·84	6·92	6·85	..	..	5	5	6·67
Nitrogen ..	..	..	..	19·24	18·36	1	14	18·67
Oxygen....	..	..	..	..	..	4	32	42·66
							75	

leading to the formula $C^4 H^4 NO^3 HO$.

Neutral Hydrochlorate of Glycocoll, Gl, HCl, HO.—This salt is obtained, as above stated, on boiling hippuric acid with hydrochloric acid. When the filtered solution is carefully evaporated to the consistence of a syrup, and then quietly left to cool, the entire liquid

becomes filled with long thin prisms, which are perfectly transparent, and possess considerable lustre. By pouring off the liquid and rinsing the crystals with alcohol, they are obtained perfectly pure. A further quantity of crystals may be obtained from the mother-ley by evaporation. On exposure to the air, the salt gradually absorbs moisture and deliquesces; the crystals however keep for a long time over sulphuric acid; their taste is acid and faintly astringent; they dissolve readily in water and spirit, and slightly in absolute alcohol. On analysis they yielded—

Carbon ..	21·11	21·28	..	..	..	4	=24·0	21·42
Hydrogen	5·96	5·95	..	..	..	6	6·0	5·35
Nitrogen	..	..	12·57	..	..	1	1·0	12·56
Oxygen ..	..	..	..	..	..	4	32·0	28·53
Chlorine..	..	..	..	31·91	31·99	1	35·4	32·14

Basic Hydrochlorate of Glycocoll, I. 2Gl, HCl, HO.—This salt is obtained when hydrochloric acid is added to a concentrated solution of glycocoll in water prepared in the cold, and then alcohol added until the solution is rendered slightly turbid. Very soon crystals of the greatest transparency and regularity are formed; to further the crystallization, a little alcohol is added from time to time, or it is perhaps preferable to allow the aqueous solution to evaporate slowly over sulphuric acid, when crystals of larger size and remarkable beauty are obtained. They are rhombic prisms of 87° and 93°; they do not deliquesce in the air like the preceding salt, and have an agreeable acid, and at the same time sweet taste; their solution reddens blue litmus-paper. The author obtained on analysis 27·59 C, 5·52 H, 15·37 N, and 19·58 per cent. Cl. The calculation requires 19·95 per cent. chlorine.

Basic Hydrochlorate of Glycocoll, II. 2(Gl, HO) + HCl.—This salt was obtained by dissolving glycocoll in muriatic acid and crystallizing. It yielded, on combustion with chromate of lead, 26·08 C, 6·02 H, and 18·53 Cl.

Basic Hydrochlorate of Glycocoll, III. 3Gl + 2HCl + 2HO.—This salt was prepared in the same manner as the preceding; an aqueous solution of glycocoll was mixed with an excess of hydrochloric acid, and set aside to crystallize; the author also obtained it by passing gaseous hydrochloric acid over fused sugar of gelatine. $1\frac{1}{2}$ grm. of substance was distributed in a Liebig's drying apparatus along the side of the tube, and slowly heated over a spirit-lamp, while a current of hydrochloric acid gas was passed over it. Between 302° and 338° the glycocoll melts in the atmosphere of acid gas. The absorption of the gas is accompanied by a disengagement of water. The operation was continued as long as the apparatus, freed from hydrochloric acid, increased in weight. The glycocoll generally became slightly green, probably owing to a trace of decomposed substance; the salt obtained according to the first method yielded 24·59 per cent.; that according to the second method, 24·23 chlorine; theory requires 24·51.

Basic Hydrochlorate of Glycocoll, IV. 3Gl + 2HCl + HO, was

prepared, like the preceding, by crystallization from an acid solution, and also by passing hydrochloric acid gas over melted sugar of gelatine. I. contained 25·43, and II. 25·72 per cent. chlorine; theory requires 25·57.

Anhydrous Sulphate of Glycocoll, Gl, SO^3.—When glycocoll is dissolved in hot spirit, and after cooling sulphuric acid added slowly by degrees, and then the whole set aside, beautiful long thin prisms or tablets are formed in the course of a day or two. The salt is soluble in water and in hot spirit, but wholly insoluble in absolute alcohol and æther; it has an acid taste, and reddens blue litmus-paper, is not altered by exposure to the air, and does not lose in weight at 212°. On analysis it yielded—

Carbon ..	22·55	22·40	22·30	..	..	4 =	24	22·66
Hydrogen	5·41	5·72	..	..	..	4	4	3·77
Nitrogen	..	..	..	13·05	..	1	14	13·20
Oxygen..	..	..	..	..	..	3	24	22·64
Sulphuric acid		..	..	..	37·97	1	40	37·73

The difference between the calculated and found quantity of hydrogen is undoubtedly owing to some sulphurous acid being absorbed by the chloride of calcium.

Hydrated Sulphate of Glycocoll, Gl, SO^3, HO.—This salt was obtained like the preceding, except that the solution was boiled with the sulphuric acid. It crystallizes in short prisms, resembling the sulphate of copper, which although small are remarkably beautiful and perfect; on analysis 12·37 per cent. nitrogen was obtained; theory requires 12·17.

Basic Sulphate of Glycocoll, a. 3Gl, HO, $2SO^3$, HO.—When sulphuric acid is added in excess to a solution of glycocoll in weak spirit, long, rectangular, prismatic crystals are formed at the bottom of the vessel in the course of 24 hours. The form of the crystals is not altered even by a large excess of sulphuric acid; they have an acid taste and reaction, are not altered in the air, and consist of—

Carbon....	22·91	22·25	..	..	..	..	12 =	72	22·29
Hydrogen..	5·68	5·56	..	..	..	..	17	17	5·26
Nitrogen ..	..	..	13·31	..	..	..	3	42	13·00
Oxygen....	..	..	..	..	..	..	17	112	34·69
Sulphuric acid ..		..	..	24·62	24·20	24·40	2	80	24·76

The following is perhaps the rational formula for this salt:—

$$(Gl, HO, SO^3, HO + Gl, HO) + (Gl, HO, SO^3, HO).$$

Basic Sulphate of Glycocoll, b. 3Gl, $2SO^3$ + HO.—The formula for this salt differs from that of the preceding by the amount of water. As both were dried over sulphuric acid without experiencing any alteration, this distinction must undoubtedly be owing to a difference in the degree of concentration or of temperature at its formation.

Basic Sulphate of Glycocoll, c. 3Gl, HO + $2SO^3$, HO.—A mixture of the solution of the salt *b* with the salt *a* afforded crystals which yielded on analysis 25·65 per cent. sulphuric acid.

Glycocoll and Sulphate of Ethyle, Gl, HO + AeO, SO^3.—This salt yielded 17·27 per cent. sulphuric acid; the formula requires 17·62 per cent.

Nitrate of Glycocoll, Gl, HO + NO^5, HO.—Dessaignes obtained this combination directly from hippuric acid, by decomposing it with nitric instead of muriatic acid. The author prepared it by dissolving glycocoll in nitric acid, and placing it over sulphuric acid. Often large tabular crystals, belonging to the monoclinometric system, were formed, but more frequently acicular crystals, especially when the liquid had been heated; they do not become moist on exposure to the air, and have an acid taste and reaction; they yielded on analysis,—

Carbon	17·86	17·13	..	4 =	24	17·38
Hydrogen	4·83	4·59	..	6	6	4·32
Nitrogen.....	..	..	20·50	2	28	20·29
Oxygen	..	..	..	10	80	58·01

Oxalate of Glycocoll, Gl, $\overline{O}$, HO.—An aqueous solution of glycocoll, evaporated with oxalic acid upon a watch-glass, crystallizes in a radiate form like wavellite. If alcohol is added to a solution of glycocoll in an excess of oxalic acid, it becomes milky, and deposits oxalate of glycocoll. When the alcohol is added by degrees in very small quantities, very beautiful crystals are formed. Dessaignes obtained this salt directly from hippuric acid, by employing oxalic acid for its decomposition. It experiences no alteration from exposure to the air.

Acetate of Glycocoll, Gl, HO + $\overline{A}$, HO + HO.—This salt is obtained by dissolving glycocoll in acetic acid, and gradually adding alcohol until the solution becomes turbid; this is repeated from time to time as the crystallization progresses. On analysis it yielded—

Carbon	33·33	8 =	48	33·33
Hydrogen.....	7·57	10	10	6·94
Nitrogen	..	1	14	9·70
Oxygen.....	..	8	64	50·03

Tartrate of Glycocoll.—When glycocoll is dissolved in tartaric acid, and absolute alcohol added in excess, an oily mass separates, which is not altered by repeated agitation with alcohol and æther. The oil dried upon a watch-glass to a gummy mass.

Palmitate of Glycocoll.—A solution of palmitic acid and glycocoll in hot spirit separates on cooling into two layers, of which the upper one is at first oily, but subsequently becomes solid, while a salt crystallizes from the lower one in white silky laminæ. The upper solid layer was easily removed; the residuary crystals were pressed between silk and dried over sulphuric acid, but their analysis led to no satisfactory formula.

Glycocoll and Chloride of Platinum, Gl, $PtCl^2$ + 2HO.—When a concentrated solution of chloride of platinum with excess of hydrochloric acid is poured into an aqueous solution of glycocoll, and then absolute alcohol gradually added, the mixture becomes turbid,

and after a short time regular cherry-red crystals are found adhering to the sides of the vessel; groups of prismatic crystals are likewise obtained on evaporating the aqueous solution over sulphuric acid. By exposure to the air they become of a lighter colour at the surface, evidently owing to a loss of water.

Glycocoll and Chloride of Barium, Gl, BaCl, 2HO.—To prepare this compound, equal equivalents of chloride of barium and glycocoll were dissolved in the least possible quantity of hot water, when upon slow cooling groups of prismatic crystals separated. They are obtained in the form of thin flat needles by adding alcohol to the solution. The salt dissolves more readily in hot than in cold water, has a bitter taste, no action upon vegetable colours, and is not altered by exposure to the air. It gave 55·34 per cent. BaCl; theory requires 55·31.

Glycocoll and Chloride of Potassium, Gl, KCl, was obtained by dissolving glycocoll and chloride of potassium in water, and evaporating over sulphuric acid. When the liquid had become very concentrated, it was entirely filled with minute needles, which readily became moist in the air. On combustion the author found 16·58 per cent. carbon; theory requires 16·92.

Glycocoll and Chloride of Sodium.—A concentrated aqueous solution of glycocoll and chloride of sodium gave, on being mixed with absolute alcohol, crystals which contained both constituents.

Glycocoll and Perchloride of Tin.—When glycocoll is dissolved in the least possible quantity of water, crystals are formed after some time which contain both constituents.

Glycocoll and Muriate of Berberine is obtained by adding an excess of a concentrated solution of glycocoll in spirit to a hot solution of muriate of berberine in the same solvent; the entire mass solidifies on cooling, and then consists of an innumerable quantity of minute orange-coloured needles. It is washed in water, which removes the free glycocoll, but in which the berberine salt is insoluble. It yielded on analysis—

Carbon	60·80	46 =	276·0	60·21
Hydrogen	5·87	23	23·0	5·03
Nitrogen	..	2	28·0	6·10
Oxygen	..	12	96·0	20·94
Chlorine.....	..	1	35·4	7·72

The formula of the compound is $C^4 H^4 NO^3$, $C^{42} H^{18} NO^7 + HCl$.

Glycocoll and Potash crystallizes in long slender needles, which readily deliquesce in the air; their solution has a strong alkaline reaction. Glycocoll also forms a crystalline compound with hydrate of baryta.

Glycocoll and Oxide of Copper may be obtained by mixing aqueous solutions of glycocoll, sulphate of copper and potash, and then adding alcohol, or by dissolving hydrated oxide of copper in an aqueous solution of glycocoll, and then adding alcohol, which when the solution is very concentrated throws down the whole of the salt. The combination lost after several days at 212°, 8·04 per

cent. = 1 equiv. HO; at the same time the blue colour gradually changed into green and violet. The analysis of the dried salt gave—

Carbon	21·54	20·66	..	..	..	4 =	24·0 20·92
Hydrogen	4·65	4·99	..	..	..	5	5·0 4·35
Nitrogen	..	..	12·65	..	..	1	14·0 12·20
Oxygen	..	..	..	..	..	4	32·0 27·92
Oxide of copper	..	..	..	33·85	33·92	1	39·7 34·61

The combination examined by Boussingault, $C^4 H^4 NO^4 CuO$, is formed by the loss of 1 atom HO = 7·84 per cent.

Glycocoll and Oxide of Lead.—This salt was obtained by dissolving oxide of lead in a boiling aqueous solution of glycocoll, and then adding absolute alcohol until it began to grow turbid. In the course of a few hours prismatic crystals formed, which bear a great resemblance to the percyanide of mercury. They contained 57·60 per cent. PbO; the formula Gl, PbO, HO requires 59·00.

Glycocoll and Oxide of Silver.—Oxide of silver dissolves readily on the application of heat in a solution of glycocoll; by the addition of alcohol the compound is obtained in warty crystals, which become black by exposure to light. Boussingault analysed this salt dried at 212°.

Glycocoll and Nitrate of Silver.—The crystals of this combination, which are obtained by double decomposition, explode violently when heated; they absorb moisture from the atmosphere. They contained 49·83 per cent. oxide of silver; calculation gives 49·53.

Glycocoll and Bisulphate of Potash, Gl, SO^3 + Gl, KO, SO^3.—When a solution of bisulphate of potash is added to a solution of glycocoll, transparent prismatic crystals are obtained on the addition of alcohol, which contain 30·94 per cent. SO^3.

Glycocoll and Urate of Ammonia, Cl, $\overline{U}$ + AmO, $\overline{U}$.—When a hot filtered solution of urate of ammonia is added to glycocoll soon after the cooling of the liquid, long semitransparent needles are formed, which adhere to the sides of the vessel. Upon the addition of alcohol a second crop of crystals is obtained. By dissolving equal equivalents of glycocoll and urate of ammonia in hot water, a flocculent mass subsides on cooling, the quantity of which is increased by the addition of alcohol, and appears under the microscope to consist of a tissue of minute prisms; it yielded 32·46 per cent. carbon and 4·40 hydrogen.

Products of Decomposition of Glycocoll.—Action of Sulphuric Acid.—Since glycocoll contains the elements of the fumarate of ammonia, $C^4 H^4 NO^3 = C^4 HO^3 NH^3$, it was conceived that it might be decomposed into these constituents; however, it was not possible to expel ammonia by baryta or by potash. When glycocoll is dissolved in dilute sulphuric acid evaporated to a syrupy consistence, and this operation repeated several times, the entire mass is converted, at a certain period not yet accurately ascertained, into beautiful crystals, which after being washed with alcohol and pulverized disengage ammonia upon the addition of potash. Some of the crystals were perfect cubes, resembling the crystals of chloride of

sodium; others were more rhombic, with pinnate margins; they have an acid taste and reaction, and are not altered by exposure to the air. Dried over sulphuric acid they gave—

Carbon	12·87	..	..	..	4 =	24	12·63
Hydrogen	5·42	..	..	..	10	10	5·25
Nitrogen	..	14·40	14·63	..	2	28	14·73
Oxygen	..	..	..	..	6	48	25·04
Sulphuric acid	..	..	..	41·85	2	80	42·10

which lead to the formula $C^4 H^4 NO^3, SO^3, HO + NH^4 O, SO^3, HO$. It was not improbable therefore that this decomposition might be brought about by a galvanic current. The solution was separated by a membrane from the water. On closing the current by immersing the poles provided with slips of platina, the one into the solution of the glycocoll, the other into the water, bubbles of gas were instantly disengaged at both poles. When the action had continued for a short time, the liquid round the negative pole was alkaline, that at the positive, acid. It can scarcely be doubted, therefore, that glycocoll is a salt the base of which is ammonia, and whose acid possesses a formula resembling that of fumaric acid. In order to obtain this acid, glycocoll was treated for several hours at a gentle heat with sulphuric acid, now and then restoring the water which had evaporated. Upon this the greater portion of the sulphuric acid was precipitated by oxide of lead, and the last portions with barytic water. The filtered liquid was concentrated by evaporation, and placed over sulphuric acid. In a few hours beautiful rhombic prisms had formed, which dissolved with difficulty in cold water, and were perfectly insoluble in æther and alcohol. With potash they disengaged ammonia, but their analysis did not afford any satisfactory results.

Action of Chlorine.—When a current of chlorine is passed through a concentrated solution of glycocoll, it is rapidly absorbed with disengagement of an abundant quantity of carbonic acid. Heat and the light of the sun facilitate the action. A Liebig's potash apparatus was filled with a solution of glycocoll, and a slow current of chlorine transmitted through it, so that the whole was entirely absorbed; at the end of the third day the process was discontinued, and the liquid evaporated to the consistence of a syrup. One drop of it, neutralized with ammonia and treated with chloride of barium or chloride of calcium, gave a white crystalline precipitate. The liquid was therefore saturated with baryta, filtered, and mixed with absolute alcohol. The precipitate was collected on a filter and washed with alcohol, when it appeared that only a small quantity of glycocoll had been decomposed. The liquid was consequently again conveyed into the potash apparatus, and a slow current of chlorine passed through it uninterruptedly for eight days, but even then some glycocoll had remained unaltered. Chloride of barium yielded with a concentrated solution, after neutralization with ammonia, a precipitate which dissolved in water. It likewise dissolved in nitric acid, but was now no longer thrown down by ammonia. After washing

and drying, the barytic precipitate was scarcely at all soluble in water even on long boiling. It contained neither chlorine nor nitrogen. On analysis the barytic compound gave the following results:—

Carbon	13·08	3 =	18·0	12·36
Hydrogen	1·89	3	2·0	2·05
Oxygen	33·38	6	48·0	32·99
Baryta	51·65	1	76·6	52·60

The same body, $C^3 H^3 O^6$, was formed on long-continued and repeated boiling of a solution of sugar of gelatine with nitric acid. By gradually adding powdered chlorate of potash to a solution of glycocoll in muriatic acid, slow oxidation takes place, and a product is obtained which yields, as in the preceding cases, the same white crystalline precipitate with baryta.

When a solution of glycocoll is heated with potash, a brilliant red colour is produced. On further concentration ammonia and hydrogen are given off until the mass becomes solid. Upon the addition of muriatic acid, prussic acid is set free and prussian blue precipitated when a salt of iron is present. The aqueous solution yielded with chloride of calcium a white precipitate, insoluble in acetic acid, and which proved to be oxalate of lime.

Considering the very numerous combinations into which glycocoll enters, the question respecting its constitution appears a difficult one to determine; sometimes it acts the part of an acid, sometimes that of a base; sometimes it behaves like a halogen salt, sometimes like a binary salt, &c.; and consequently it must be arranged in all these classes, for it possesses all the properties by which each of these classes is distinguished from the others.

Since glycocoll is a constituent of hippuric acid, the author concluded his researches with a physiological experiment. After having convinced himself of the absence of free glycocoll in the urine, he took 4 grms. of it, but not a trace could be detected in the urine; the quantity of urea and uric acid, however, was increased. —Liebig's *Annalen*, lx. p. 1.

On the Production of a Substance analogous to Gun-Cotton from Glycerine. By A. Sobrero.

When a mixture of 2 vols. of sulphuric acid of 1·83 and 1 vol. nitric acid of 1·43 is poured into syrupy glycerine, a very lively oxidation ensues, the products of which I have not ascertained; if, on the contrary, the above mixture of the two acids is placed in a freezing mixture, and glycerine poured into it, agitating to avoid all elevation of temperature, the glycerine quickly dissolves without any perceptible reaction; if the mixture be now poured into water, an oily substance heavier than water subsides to the bottom of the vessel, where it is washed with a considerable quantity of water, to free it entirely from acids without any loss, as it is quite insoluble in that menstruum. When well-washed, it is wholly dissolved in alcohol, and precipitated again by water or dissolved in æther, and the solution left to spontaneous evaporation, when it is obtained in a state

of perfect purity. It is readily freed from water by keeping it for a few days *in vacuo* over sulphuric acid.

In this state this body has the appearance of olive oil coloured slightly yellow; it has no odour; its taste is sweet, pungent and aromatic; but in making this experiment great precaution should be used, for a very minute quantity held upon the tongue produces a violent headache for several hours. This effect upon the human body was experienced by several persons in my laboratory, and I have frequently felt its effects myself.—*Comptes Rendus*, Feb. 15, 1847.

On the Decomposition of Water by Platina and Black Oxide of Iron. *By* Dr. George Wilson.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—In your last Number you are so good as to publish an abstract of a paper of mine, read to the Chemical Society, "On the Decomposition of Water by Platina and Black Oxide of Iron." The statement of the experiments and their results is in all essential particulars quite accurate; but the author of the abstract has misapprehended my views as to Mr. Grove's theory of the decomposition of water by a white heat. I shall feel much obliged, therefore, if you will spare me space enough in your next Number to correct the mistake (doubtless accidental) which has been made.

The following is the passage on which I wish to comment. The italics in the last word are my own:—

"Dr. Wilson then argues, that the decomposition of water by a white heat may be referable to the mechanical disruption of the particles in direct contact with the heating body, and not to the decomposing power of heat alone; as the statement that water can be produced by the same processes that disunite its elements would be tantamount to affirming that unlike effects may flow from the same cause, without any alteration in the qualities or conditions of the *water*. [For *water* read "cause."]

On the first part of the preceding passage (*i. e.* down to the semicolon) I have to observe, that I have not argued that Mr. Grove's results are explicable on the supposition that compound bodies raised to a white heat are exposed to a disruptive force, which can disunite their elements; neither have I refused to believe, along with the gentleman in question, that heat alone is the cause of the decomposition of water, observed in his experiments with white hot platina. On the other hand, I have distinctly stated that I hold the opinion, that the white heat alone produced the resolution of water into hydrogen and oxygen. My remarks as to mechanical disruption were limited to the experiments made with Leyden jar discharges, and applied to the disruptive force of the discharge, not to that (if there be any) of the heat of the discharge. They were offered in bar of Mr. Grove's conclusion, that the spark-decompositions were referable solely to the heat of the electric sparks, and might therefore be considered as crucial. I suggested, on the other hand, that there were three decomposing agencies possibly at work

in every electric discharge,—1st, an electric (though not an electrolytic) one; 2nd, a mechanical disruptive force; and 3rd, the decomposing power, proper, of the heat of the spark. On the second I particularly dwelt, as certainly possessed by electric discharges, and competent to effect chemical decomposition; perhaps even that of water. I did not, however, deny the proper decomposing power of the heat of the spark; still less did I extend these conclusions to experiments made with platina simply heated. My object, on the other hand, was to show that the spark experiments were not *experimenta crucis*, but more complicated than the platina trials, which I accordingly discussed apart from them. It is matter of certainty that water (liquid or gaseous) exposed to electric discharges is subjected to a powerful disruptive force. Whether water heated white-hot is acted on by a disruptive force is not a point on which, in the paper under notice, I have expressed any opinion.

The latter half of the paragraph I have quoted is rendered unintelligible by the sentence being closed with the word "*water*" instead of "cause." Read with this alteration, it expresses an opinion contained in the paper, but one which is not connected, as the preceding statement will show, with any denial of the power of heat to decompose water. The declaration in question took for granted that heat can decompose water, but was opposed to the view that Mr. Grove's experiments show, that the same (*i. e.* in all respects the same) heat which combines oxygen and hydrogen into water can decompose water into those bodies. It was argued, on the other hand, that the heat which produces combination in the case under notice is of very low intensity compared with that which causes decomposition. In strictness of language, therefore, it cannot be said, so far as heat is concerned, that "water can be produced by the *same* processes which disunite its elements;" for the difference in *intensity* of the heat that combines, as contrasted with the heat that decomposes, renders the processes *not* the same. The combining heat is a very low red heat; the decomposing heat a very high white one.

I remain yours very sincerely,

Laboratory,
24 Brown's Square, Edinburgh,
May 5, 1847.

GEORGE WILSON.

Examination of a Roman Glass. By M. GIRARDIN.

In one of two Roman tombs, which were discovered in constructing a road, were found some fragments of a beautiful white glass vessel, which was remarkable for its great weight. The author found it to contain a pretty considerable quantity of lead with a trace of copper, just as the crystal glass of the present day prepared with litharge. It appears from this that the manufacture of lead glass was known to the ancients, although they make no mention of it. In the examination of another blue glass of extraordinary beauty, derived probably from an Etruscan tomb, the author found it to be coloured with cobalt. Davy likewise found cobalt in an antique

blue glass. The ancients, it appears, looked upon cobalt as a species of copper, an error which was first exposed by G. Brandt in 1742. Another blue glass found in France was, on the contrary, coloured with the *Cæruleum* of Vitruvius.—*Journ. de Pharm. et de Chim.*, x. p. 321.

On the Products which are formed in the Dry Distillation of the Cinnamate of Copper. *By* C. W. Hempel.

The author found the following process for preparing cinnamic acid to be the most advantageous:—Storax is boiled for an hour with an excess of caustic potash diluted with water, and the liquid decanted on cooling. This operation is repeated. The solution of cinnamate of potash and resin is precipitated with hydrochloric acid, the precipitate collected, and then boiled with water in a copper pan. The hot liquid is separated from the residuary resin by straining through a piece of linen, and on cooling deposits impure cinnamic acid. This is again dissolved in caustic potash, and hydrochloric acid added to the solution until the precipitate produced assumes a very pale brown colour. The liquid separated from the precipitate is now thrown down entirely, the precipitate again dissolved in water and left to crystallize, when, after rinsing, perfectly pure cinnamic acid is obtained.

To prepare the cinnamate of copper, the solution of the potash salt was thrown down with sulphate of copper; the bluish-white precipitate was dried at 212°, and submitted to distillation. At about 302° decomposition began with evolution of carbonic acid and some carbonic oxide, while a clear liquid passed over; at about 356° some crystals adhered to the neck of the retort, the quantity of which rapidly increased at a still higher temperature, but were all partially redissolved by the oil, which passes over along with it. At about 482° the entire mass in the retort became liquid. The distillation was continued until the residue again became dry.

The crystalline product was treated with a solution of carbonate of soda, then precipitated with hydrochloric acid, the precipitate washed, dissolved in boiling water, and allowed to crystallize. The crystals were again recrystallized from water, and then dried at 212°. Analysis showed that they consisted of cinnamic acid. The liquid which had passed over was treated with dilute caustic potash, to remove any cinnamic acid it might contain, washed with water and rectified; a residue was left in the retort, which on cooling entirely solidified, and did not dissolve on treatment with æther and alcohol. This led the author to suppose that the solidified mass consisted for the greater part of metastyrole and the rectified liquid of styrole; an excess of bromine was therefore placed in contact with the latter, when the entire mass solidified in a short time to crystals possessing the properties of bromostyrole. The solidified mass yielded on analysis 92·10 per cent. carbon and 7·98 hydrogen; it was therefore really metastyrole, which requires 92·30 C and 7·70 per cent. H. Besides the bodies above-mentioned, a crystalline mass, insoluble in

carbonate of soda, but which could be crystallized from alcohol, was obtained at the same time as the cinnamic acid. The crystals obtained were colourless, prismatic, readily soluble in alcohol and æther, but insoluble in a solution of caustic potash; they melted far below 212°, and then solidified to a radiately-crystalline mass. They probably consisted of benzoyle, for this dissolves like them in sulphuric acid, and possesses a similar odour.

Cinnamate of copper likewise yields styrole on distillation, but the decomposition is rather complex; the hydrate water of the acid is wanting in this salt, and other bodies are formed. The styrole is produced by the cinnamic acid being decomposed into carbonic acid and styrole, as proved by the following experiment.

The vapour of cinnamic acid was passed through a glass tube filled with fragments of glass, and heated to a faint red heat; a dark brown liquid formed, which was rectified over water; the product was colourless; when a glass bulb was filled with it and sealed, and exposed to the temperature of boiling water, it solidified with the greatest ease; it was consequently pure styrole. When a higher temperature is employed, a mixture of different hydrocarbons is obtained, and the liquid can no longer be rendered solid.—Liebig's *Annalen*, lix. p. 316.

On the Decomposition of the Iodide of Antimony and Iodide of Arsenic. *By* M. Buchner, Jun.

According to Brandes, the iodide of antimony (SbI^3) is decomposed by water into a basic protiodide (Sb^2I), which separates as a yellow powder, and an acid compound, which remains in solution; the author maintains, on the contrary, that the decomposition entirely corresponds to that of the chloride of antimony, a combination analogous to algaroth powder is eliminated, and hydriodic acid left in solution. In examining this powder, potash must not be employed, because this dissolves a portion of the oxide of antimony, which may, it is true, be again precipitated by acidifying the solution; but it is then always accompanied with some iodine, to which it owes its yellow colour. Ammonia, on the contrary, decomposes this compound even in the cold, the whole of the antimony separating as white oxide, while the iodine remains as iodide of ammonium in the liquid. It is best to dilute the liquid, in order that the whole of the antimony may separate, and to warm it gently until the excess of ammonia is expelled; the iodine may then be readily determined by precipitating the filtered solution with nitrate of silver. To estimate the antimony, the author fused the eliminated oxyiodide with cyanide of potassium, when the antimony is reduced; taking care, however, before fusing the powder with cyanide of potassium, to moisten it with some potash ley, in order to avoid the volatilization of a portion of the periodide of antimony. A long-continued faint red heat is requisite for the reduction to succeed, as otherwise some oxide of antimony might remain undecomposed. The powder was found to possess the following composition:—

Antimony.....	60·30	60·46	6 =	9677·4	60·73
Iodine	29·93	29·54	3	4756·5	29·85
Oxygen.....	..	..	15	1500·0	9·42

This leads to the formula $SbI^3 + 5(SbO^3)$, which is analogous to the formula for algaroth powder, $SbCl^3 + 5(SbO^3)$, according to Duflos. However, as with algaroth powder, the composition of the oxyiodide of antimony is not perfectly constant with different modes of preparation, as indicated by a difference in the colour; thus a somewhat red-coloured sample gave 60·27 per cent. Sb and 31·81 per cent. I. The first oxyiodide is always formed when the periodide of antimony is not triturated with too large a quantity of cold water, and then washed with cold water; when the periodide is at first treated with but little and hot water, the basic compound appears to acquire a deeper colour. When the periodide of antimony is immediately treated with a large quantity of water, a very light powder remains, which may be seen by the naked eye to be a mixture of oxyiodide of antimony and oxide of antimony. The yellow body which is produced by the action of iodine upon tartar-emetic is likewise an oxyiodide of antimony; this also varies in composition.

The iodide of arsenic (AsI^3) experiences a similar decomposition by water as the iodide of antimony; but in this case the eliminated compound, which is constantly decomposed more and more on the continued washing with water, could not be analysed.—Buch. *Rep.*, xliii. p. 357.

ANALYTICAL CHEMISTRY.

Description of a new Process for estimating Gold. By O. Henry.

M. Barral, in an excellent investigation upon the precipitation of gold *, has explained in a very ingenious manner what happens in gilding by immersion in the process patented by Mr. Elkington. The terchloride of gold, $Cl^3\,Au^2$, mixed with bicarbonate or sesquicarbonate of potash, and in the presence of copper, is converted either into protochloride of gold, $ClAu^2$, or into deutochloride of gold, $Cl^2\,Au^2$, which is then decomposed progressively so as to fix upon the object to be gilt the gold Au^2, while 2 equivs. of copper Cu^2, combine with the chlorine Cl or Cl^2, to form a protochloride or deutochloride of copper. The potash then removes either Cl^2 in the first case, or Cl in the second, and forms 1 or 2 equivs. composed of chloride of potassium, hypochlorite and chlorate of potash. The eliminated carbonic acid is disengaged; and as this acid exerts no action upon the gilding, the operation progresses without interruption.

It is possible that the addition of an alkaline salt, or of a readily decomposable salt the acid of which would not act upon the gold mixed with the terchloride of gold, $Cl^3\,Au^2$, would facilitate the precipitation of this metal upon the copper, yielding to the portion

* Chem. Gaz., vol. iv. p. 326.

of chlorine eliminated from the terchloride the base to saturate it and produce new compounds. So much is certain, that in a mixture of terchloride of gold, a basic salt and copper, a quantity of copper equivalent to that of the gold, separated either in powder or upon the object to be gilt, is dissolved. It is upon this principle that is founded the process of analysis which we propose to determine the quantity of gold fixed upon a gilt object, that of an alloy, or of a gold solution submitted to examination. Having been engaged for two years, conjointly with MM. Chevalier and Barral, in a great number of judicial investigations relative to the new processes of gilding and silvering of MM. Elkington and Ruolz, we have had to analyse many gilt objects, or solutions employed for gilding, which have been seized. We have frequently experienced the difficulty of appreciating very minute quantities of gold, either by weighing or by cupellation, which requires long and difficult operations. To avoid these inconveniences, I have imagined a process for estimating the gold indirectly by means of standard solutions, and which I shall now proceed to describe.

When the amount of gold upon a gilt object, or in a bath which has been or is to be employed for gilding, has to be ascertained, the following plan may be adopted:—

1. The objects, weighed with care, are digested with hot pure nitric acid; as soon as the copper forming the basis is dissolved, the solution is diluted with distilled water, and the gold is soon seen to settle at the bottom of the vessel in small brilliant scales*. These are collected, and after washing dissolved in *aqua regia*, the solution evaporated with great precaution nearly to dryness, so as to obtain a ruby-red product soluble in water; this is the terchloride of gold with a little acid. This product is now dissolved in distilled water, and mixed with 5 or 6 times its weight of pure bicarbonate of potash or soda dissolved in distilled water; the mixture is heated, conveyed into a ground-stoppered flask, and a somewhat large amount of finely-divided copper, which has been previously heated in a current of hydrogen, added to it; the mixture is now and then shaken, and after about an hour the liquid assayed. A very minute quantity of the liquid is poured upon a watch-glass, and treated with protosulphate of iron; if the liquid does not yield a black or gray precipitate, it is a sign that it contains no gold in solution; should the contrary occur, more copper must be added, and again agitated. When the whole of the gold has been precipitated upon the copper, the liquid is carefully saturated with pure sulphuric acid so as to be *slightly acid*. By this means all the copper precipitated in the state of *carbonate* is dissolved without the gold or *metallic copper* being at all acted upon: it is filtered, and a solution of pure ferrocyanide of potassium of 40° † carefully added by

* Sometimes the separated gold retains the form of the object, especially if the gilding is at all thick.

† The solution of ferrocyanide of potassium of 40° is obtained by dissolving 1 grm. in 10 grms. of water, and adding to the mixture sufficient water to make 40 grms. This solution must not be prepared too long in advance, and should be preserved in a stoppered bottle.

drops to the liquid, employing for this operation the instrument described by M. Dupasquier under the name of sulphydrometer; the addition is continued until a precipitate ceases to be formed*.

The number of divisions of the instrument employed to precipitate exactly the whole of the copper is noted down, and in this manner the quantity of the metal dissolved in the liquid ascertained.

100 measures of this liquid of the strength described represent 0·360 grm. copper, which is equivalent to 0·146 grm. gold; consequently 1 measure of the instrument described represents 0·0036 copper and 0·00146. metallic gold.

2. When it is a solution which is to be, or has been used for gilding, I advise precipitating the diluted acid solution by a current of sulphuretted hydrogen, collecting the precipitate, and strongly calcining it after washing. The sulphuret of gold being reduced to the metallic state, the calcined residue is redissolved in nitric acid, and the gold which has remained unattacked dissolved in *aqua regia*, and treated as above described.

The use of the ferrocyanide of potassium to determine the amount of copper which represents the gold in a compound, is founded on the fact that this reagent is still very sensitive when the hydrosulphate of soda has no longer any perceptible action. 0·001–0·0005 of copper in solution are precipitated by the ferrocyanide of potassium, whilst the hydrosulphate scarcely produces a slight brownish tint.

To show the advantages of this process, the following experiments were made:—2 grms. of pure copper, dissolved in pure nitric acid, then evaporated to expel the excess of acid, and treated with distilled water, yielded a perfect solution, which was precipitated by the ferrocyanide of potassium, and consumed the following measures of the sulphydrometer:—

1. With 0·2 copper, 79·2 measures of ferrocyanide.
2. With 0·05 copper, 19·8 measures.

I then took 2 grms. of thin leaf-gold, which were dissolved in *aqua regia*, evaporated to drive away as much as possible the excess of nitromuriatic acid, and mixed with its solution a large quantity of distilled water; this was then divided into several parts, A, B, C; of which A contained 0·250 metallic gold; B, 0·150; and C, 0·100; to each portion bicarbonate of potash and pure finely-divided copper were added as above described, and after filtration of the slightly acid solution, tested with a normal solution of ferrocyanide.

* The sulphydrometer which I use for these experiments is a straight glass tube, with a glass stop-cock cemented to it, and terminated by a drawn-out point. By this arrangement, it is very easy to add the test-liquor drop by drop.

The precipitate is allowed to subside, or it is better to filter it, taking care to mix previously with the liquid some pure chloride of sodium, in order to hasten the separation of the ferrocyanide of copper. The excellent method described by M. Pelouze may also be employed to ascertain the amount of copper; however, as will be subsequently shown, the ferrocyanide is far more sensitive, which has led me to give it the preference.

A required on an average	31·3000	measures.
Corresponding to metallic gold ..	0·2510	...
B required on an average	18·7000	...
Corresponding to gold	0·1503	...
C required on an average	12·5000	...
Or metallic gold	0·1004	...

It is evident, therefore, that this process for determining the amount of gold is exact and advantageous, from the ease and quickness with which it may be performed.

Thus 100 measures of the standard solution of ferrocyanide of potassium employed in the assay will represent 0·8045 metallic gold; consequently, by means of the rule of three, the number of measures of the standard solution being given, we obtain the quantity of gold in an assay; let M, for instance, = 25, then

$$100 : 0{\cdot}8045 :: 25 : x \text{ or } \frac{0{\cdot}8045 \times 25}{100} = 0{\cdot}2011.$$

The conditions requisite for the success of the operation are,—1st, to take care that the copper employed is perfectly *free* from oxide; 2nd, to be certain that, after contact with the copper, no gold remains in solution; 3rd, to saturate the mixture exactly with pure sulphuric acid after the reaction; 4th, to mix, as quickly as possible, at a gentle heat, the copper and the bicarbonate to the solution of the terchloride of gold; 5th, to add the test liquid, which has been made shortly before use, with precaution and only by drops when but a slight chestnut or dark red precipitate is produced.—*Journ. de Pharm.*, Jan. 1847.

On the Method of separating Cobalt from Manganese proposed by Barreswil. *By* A. Strecker.

A short time since M. Barreswil* proposed a very simple method of separating these two metals, by adding carbonate of baryta to the solution containing them, and then passing sulphuretted hydrogen into it. The author, before employing it, wished to ascertain whether in reality no manganese would be precipitated, as stated by M. Barreswil, and mixed for this purpose solutions of the protochloride and of the protosulphate of manganese with pure carbonate of baryta, and passed sulphuretted hydrogen into them. It was found that nearly the whole of the manganese was precipitated, and the filtered alkaline liquid became turbid on heating to boiling, and contained now not a trace of manganese. This is readily explained by the behaviour of carbonate of baryta towards sulphuretted hydrogen. When a current of this gas is passed into water containing carbonate of baryta in suspension, a portion of it is decomposed in the same way as the alkaline carbonates, and the liquid contains a considerable quantity of baryta in solution, partly in the form of carbonate dissolved in carbonic acid, partly as hydrosulphuret of barium

* See Chem. Gaz., vol. iv. p. 159.

and hyposulphite of baryta. The very alkaline liquid is rendered turbid by boiling, with separation of carbonate of baryta, and on evaporation to half its volume constantly disengages sulphuretted hydrogen; upon the addition of muriatic acid, this gas and carbonic acid escape, and the liquid is rendered turbid by sulphur; sulphuric acid indicates the presence of a large amount of barytic salts. It is to be hoped that when M. Barreswil next imagines a method, he will test its correctness before publishing it.—Liebig's *Annalen*, Feb. 1847.

CHEMICAL PREPARATIONS.

On the Preparation of Lactic and Butyric Acids. By A. Bensch.

In the preparation of lactic acid according to the process of M. Gobley*, there is nothing to show when the metamorphosis of the sugar into lactic acid has been effected, as he employs so much water that the lactate of lime formed remains almost wholly in solution. But since the formation of butyric acid begins as soon as the production of lactic acid is terminated, a great loss of lactic acid may readily occur, which may be easily prevented by using a smaller quantity of water. The addition of tartaric acid to the solution of sugar, in order to convert the cane into grape-sugar, and the addition of stinking cheese, facilitates the formation of lactic acid, and prevents the contemporaneous production of large quantities of butyric acid.

The circumstance that the lime-salts prevent the separation of the otherwise so sparingly soluble salts of zinc and protoxide of iron, does not allow of the employment of the lime-salt in the preparation of the above salts; and I therefore prefer decomposing it with sulphuric acid, and combining the lactic acid with oxide of zinc, as the purification of the lactate of zinc and the separation of the lactic acid from it present no difficulties. The mixture which I use for the preparation of lactic acid is essentially the same as that employed by Pelouze and Gelis for the preparation of butyric acid.

Lactic Acid.—6 lbs. of cane-sugar and ½ oz. of tartaric acid are dissolved in 26 lbs. of boiling water, and set aside for some days; upon this, 8 oz. of old stinking cheese, well diffused in 8 lbs. of curdled acid milk from which the cream has been removed, are added to the above mixture along with 3 lbs. of finely-powdered chalk, the whole located in a warm place, so that the temperature of the liquid is from 86° to 95°. It is well stirred every day several times; in the course of 8 to 10 days the entire mass solidifies to a stiff paste of lactate of lime; 20 lbs. of boiling water and ½ oz. of caustic lime are added to this paste, boiled for half an hour, and filtered through a linen bag. The liquid is evaporated to the consistency of a syrup, set aside for four days, in which time the lactate of lime has sepa-

* See Chem. Gaz., vol. ii. p. 406.

rated in a granular crystalline form; it is expressed, then agitated with one-tenth its weight of cold water, again submitted to pressure, and this operation repeated two or three times.

The lactate of lime, after being expressed as well as possible, is dissolved in twice its weight of boiling water; and for every pound of expressed lactate of lime, 3½ oz. of sulphuric acid previously diluted with its weight of water added to the solution. The hot liquid is immediately filtered through a conical bag from the gypsum, and boiled with 1$\frac{3}{4}$ lb. of carbonate of zinc for every 1 lb. of sulphuric acid used for a quarter of an hour; if boiled longer, a very insoluble basic salt is formed. The solution, filtered boiling hot, soon deposits perfectly colourless lactate of zinc in crystalline crusts, which may be obtained perfectly free from sulphuric acid by rinsing with cold water. The mother-ley is again boiled with any of the salt which may have remained on the strainer, or concentrated by evaporation. It yields, nearly to the last drop, perfectly white zinc salt.

To separate the lactic acid from this salt, I dissolve it in 7½ parts of boiling water, pass a current of sulphuretted hydrogen into the hot liquid until it has become cold, and no further separation of sulphuret of zinc is perceptible. The liquid filtered from the sulphuret of zinc is boiled to expel the excess of sulphuretted hydrogen, and then evaporated in a water-bath to the consistence of a syrup. 8 parts of lactate of zinc yield in this manner 5 parts of perfectly pure syrupy lactic acid.

Butyric Acid.—When the above mixture of sugar, chalk, &c. is left longer than ten days at 95°, and the evaporated water renewed, the mass again becomes liquid, gas bubbles are given off, and in from five to six weeks the lactic acid is converted into butyric acid, and the evolution of gas ceases. The liquid is now mixed with an equal volume of cold water, and a solution of 8 lbs. crystallized soda added; the carbonate of lime collected on a filter, and well washed; the liquid evaporated to 10 lbs., and mixed cautiously with 5½ lbs. of sulphuric acid, which has previously been diluted with an equal weight of water. Butyric acid separates as a dark-coloured oily layer upon the solution of the bisulphate of soda, and can be readily separated by a separating funnel. The solution of bisulphate of soda is submitted to distillation, the product saturated with carbonate of soda, the butyric acid likewise separated after evaporation by sulphuric acid, and the crude butyric acid rectified, after the addition of 1 oz. of sulphuric acid for every pound, in order to prevent the separation of anhydrous sulphate of soda, which would cause a violent thumping. The dilute rectified butyric acid is saturated with fused chloride of calcium, which separates the acetic acid, and then again submitted to distillation. The first portion that passes is dilute butyric acid containing traces of muriatic acid; this is succeeded by concentrated butyric acid, and there is left in the retort a small quantity of chloride of calcium and brown-coloured butyric acid.

Pelouze and Gelis distilled the crude butyrate of lime with mu-

riatic acid; this operation requires very large retorts, as a violent frothing is unavoidable; moreover, by this method the butyric acid is rendered very impure by muriatic acid, two evils which are avoided by the method I have proposed. I obtained from 6 lbs. of cane-sugar 28 oz. of pure concentrated butyric acid.—Liebig's *Annalen*, Feb. 1847.

On the Purification of Mercury from Tin. *By* H. Wackenroder.

When crude muriatic acid containing a tolerable quantity of sulphurous acid is placed in contact with tinfoil at the ordinary temperature, a violent reaction takes place with disengagement of hydrogen, and the sulphurous acid is decomposed. This circumstance may be turned to account in purifying mercury from tin. The mercury containing tin, in quantities from 3 to 4 lbs., is mixed with crude muriatic acid and exposed to the sun for several days, now and then agitating. A considerable quantity of sulphuretted hydrogen and hydrogen escape; and when the acid is now digested with the metal for some hours at 176°, the latter is entirely freed from tin. Muriatic acid, which has been mixed with one-eighth of liquid sulphurous acid, may also be employed to test commercial mercury for the presence of tin. On mixing the mercury and acid together, not a trace of sulphuretted hydrogen should be disengaged, and a slip of paper moistened with acetate of lead not be blackened even when the mixture is gently heated.—*Archiv der Pharm.*, xlviii. p. 29.

On a new Method of preparing Cyanuric Acid. *By* Ad. Wurtz.

When a current of dry chlorine is passed over fused urea, a very violent reaction is perceptible; the substance is decomposed, swelling and disengaging abundant white vapours. The products of this reaction are cyanuric acid, chloride of ammonium, hydrochloric acid and nitrogen. To extract the cyanuric acid, the mass left in the vessel in which the decomposition was effected is treated after cooling with a little cold water. The chloride of ammonium is dissolved in the water, and the cyanuric acid is left in the form of a white powder, which may be purified if requisite by dissolving it in boiling water. The following equation explains the reaction of chlorine upon urea:—

$$3(C^2H^4N^2O^2) + 3Cl = N + HCl + 2H^4NCl + C^6N^3H^3O^6.$$

I may add that this is certainly the easiest method of preparing cyanuric acid*.—*Comptes Rendus*, March 15, 1847.

* This method is identical with that proposed by M. de Vry in our last Number.—Ed. *Chem. Gaz.*

THE CHEMICAL GAZETTE.

No. CXI.—June 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Berberine and some of its Compounds, with Remarks on certain Precautions which are necessary to be observed in the Determination of the Elementary Composition of similar Bodies. *By* Geo. Kemp, M.D. Cantab. F.C.P.S.

In the year 1839, during the examination of the compounds formed by carbazotic acid and the vegetable bases, in order to determine the value of that acid as a discriminative test, the writer ventured to place berberine amongst the alkaloids*; and, pursuing the subject in the following year, the muriate, acetate, sulphate, and various other salts were formed; the modes of formation communicated to Prof. Buchner, with specimens which were deposited in the Chemical Museum of the University of Munich, and the basic properties of berberine considered as fully determined. In the year 1841, the writer was requested by Prof. Liebig to pursue the subject in the Giessen Laboratory, by comparing the composition of some of the salts alluded to with that of berberine itself, as elicited by Dr. L. A. Buchner; and the results were compiled in a paper for the 'Annalen,' dated April 27, 1842. Having received a request from his venerable friend, Prof. Buchner, to withhold the communication until his son had an opportunity of re-examining the subject, the writer begged Dr. Will, to whom the paper was entrusted, to delay its publication; M. Th. Fleitmann, whose paper appeared in the 'Chemical Gazette,' No. 107, will therefore see that the discovery of the basic nature of the body in question was determined years ago, and that his claim is totally unfounded. The matter of priority, however, on such a subject is of slight importance, when compared with the fact, that the internal evidence of M. Fleitmann's paper plainly determines his views as to the composition of berberine to be incorrect; that the combining weight actually brought into comparison with the relative amount of the elements leads to a formula differing essentially from that assigned to it; and that this error has arisen from a cause pointed out in some remarks on the construction of formulæ, recently published in the 'Chemical Gazette,' p. 71 of the present volume.

* Buchner's Repertorium, 1840; Geiger's Handbuch der Pharmacie, p. 1164–1841.

Since the discovery of Prof. Liebig, that the chloride of platinum forms double salts with the muriates of most of the alkaloids, we possess an elegant and most precise mode for determining the composition of these bodies, as free from water. No error can arise, unless the solution of the chloride of platinum contains free chlorine, which in some cases produces decomposition; and as this precaution is not generally known, it may be worth noticing*. This mode of determining the composition of any organic base is peculiarly valuable, as removing all the difficulties which formerly impeded the progress of the analyst, from the circumstance that many of these bodies contain a large quantity of water, whilst the conditions under which this water is removed, both as to temperature and atmospheric pressure, are ill-determined, so that the most remarkable discrepancies occur in the analyses, which immediately become reconciled on applying the mode referred to.

The following are the analytical results of the platinum salt†:—

I. 814 milligrammes gave 147 or 18·05 per cent. platinum.
II. 437 milligrammes gave 79 or 18·07 per cent. platinum.
M. Fleitmann found 18·11 per cent. platinum.

What is usually then called the atomic weight, as deduced from these data, becomes 6831, 6822, 6808 respectively. The formula proposed by M. Fleitmann is $C^{42}H^{18}NO^{9} + HCl + PtCl^{2} = 7025{\cdot}5$, requiring a reduction of the amount of platinum found per cent. in the proportion of 18·11 : 17·55. To obtain less platinum than the body contains is possible if the combustion be conducted too hastily; to obtain more is simply absurd; any trifling difference in the second decimal may of course be referred to unavoidable errors in minute weighing.

Not to occupy unnecessary space, the following is a summary of the analyses made by the author at Giessen, with the formula which he still considers supported by the facts of the case:—

	Calculated.		Found. I.	Found. II.
42 equivs. of carbon‡	3150·00	= 46·23	46·23	46·22
18 equivs. of hydrogen ..	225·00	3·32	3·68	3·63
1 equiv. of nitrogen	177·04	2·55	2·54	2·57
3 equivs. of chlorine	1327·95	19·49	19·43	19·44
1 equiv. of platinum	1233·00	18·09	18·05	18·07
7 equivs. of oxygen	700·00	10·32	10·07	10·07
	6832·99	100·00	100·00	100·00

or $C^{42}H^{17}NO^{7} + HCl + PtCl^{2}$; the berberine itself, like brucine, contained 9 equivs. of water. The above analyses were made with

* M. Fleitmann considers that the berberine hitherto examined was either muriate of berberine or a mixture of this with berberine. It will be seen that the analysis of the platinum compound is perfectly free from any error that could thus arise.

† A very interesting mercury compound is formed by the mutual reactions of muriate of berberine and corrosive sublimate.

‡ Carbon, 75.

chromate of lead; the platinum compound of M. Fleitmann, although leading to a combining weight almost identical with the above, gave nearly 2 per cent. less carbon; and its formula, correctly deduced, is $C^{40}H^{17}NO^9 + HCl + PtCl^2$; this, at least, is the nearest approximation that the facts of the case admit of. Having now seen that the subject still challenges investigation, it may be proper to remark, that both organic acids and bases, which contain water removable at various temperatures and under different conditions, do not admit of the ordinary course pursued for the purpose of eliciting the ultimate composition of such bodies. After having performed the usual manipulations of weighing, mixing, charging the tube, &c., this last is connected with an exhausting syringe and surrounded with hot sand; no great delicacy is observed about the temperature; a bit of paper or a chip of wood, if not scorched, is presumed to indicate that the heat is not too high, and, if not a vacuum, certainly an approximation to one is now obtained by means of the syringe. In cases where a portion of water is lost at 100° C., under ordinary atmospheric pressure such a course must inevitably vitiate the analysis, and lead to erroneous results; the writer has indeed seen this apparently simple oversight the cause of much perplexity and loss of time. If the substance be dried, and mixed at a temperature decided by experiment to produce constant results, and then allowed to cool under a receiver with sulphuric acid, any error arising from the moisture suspended in the atmosphere will be very trifling, especially if a dry day be selected for such analyses. Those whose experience has proved the necessity of attention to little things in the higher departments of organic analysis, will not consider any practical remark irrelevant.

St. John's, Isle of Man, April 22, 1847.

On the Atomic Weight of Magnesia. *By* T. Scheerer.

The author decomposed the solution of a known weight of extremely pure anhydrous sulphate of magnesia with a solution of chloride of barium, and weighed the sulphate of baryta produced. He obtained in four experiments, SO^3 being taken at 500·75 and BaO at 955·29,—

			Atomic weight of magnesia.
I.	66·573 SO^3 combined with	33·427 MgO	251·43
II.	66·608	33·392 ...	251·04
III.	66·639	33·361 ...	250·69
IV.	66·592	33·408 ...	251·22

Two other experiments yielded 250·82 and 250·64; the mean of the six experiments is 250·97.

M. Gerhardt observes, that on employing the new atomic weights S = 200 Ba = 850, a somewhat lower number would be obtained for the atomic weight of magnesia; that is to say, one closely approximating to 250, which would make Mg = 150, or 12 times the equivalent of hydrogen.—*Journ. de Pharm.*, April 1847.

On the Presence of Sugar of Milk in the Milk of the Carnivora. *By* Dr. A. Bensch.

In the experiments of Dumas upon the milk of the bitch*, it was shown that the sugar completely disappeared when the food consisted entirely of flesh, whilst it was always present, and in considerable quantities, when the diet was vegetable: the following experiments however prove that this is not the case, and that the sugar is always present in the milk; also that it frequently undergoes a change from the method of analysis, which prevents its crystallization.

Two large dogs, which had pupped four days previously, were fed entirely upon meat; the pups were separated from them 6 hours before the milk was drawn. The milk reddened litmus-paper the moment it left the teat. When heated, it coagulated, forming a dense mass; on dilution with water, it lost this property, and coagulated imperfectly. When diluted with water and treated with a little acetic acid, the caseine readily separated on ebullition; the fluid is readily filtered when a small quantity of a mixture of æther and alcohol is added to it. After the evaporation of the æther and alcohol, the whey reduced persalts of copper upon the addition of potash, which indicates the presence of sugar.

On analysing it, I followed Haidlen's method†, increasing the quantity of sulphate of lime to half the weight of the milk, so as to obtain a residue susceptible of being completely dried. On drying the residue, unless special care be taken, it frequently happens that it suddenly increases in weight, probably from an energetic oxidation of the fatty matter; this amounted in one case to 30 milligrms. in the space of 6 hours. The milk of the first dog had a specific gravity of 1·036, and was acid. It yielded on analysis—

Water	75·54
Butter	10·75
Sugar and soluble salts	3·47
Caseine and insoluble salts	10·24
	100·00

The solution obtained by exhausting with alcohol the residue left after extracting the fatty matter with æther was evaporated, the residue treated with absolute alcohol, the insoluble portion dissolved in water and set aside; no crystals of sugar formed, although oxide of copper was readily reduced when potash was present. Another portion of the same milk was diluted with 3 parts of water, a few drops of acetic acid added, the mixture heated and filtered, the filtrate evaporated with carbonate of magnesia, and the dried mass exhausted with alcohol until the reaction of the magnesia disappeared; the residue on the filter exhausted with hot water, and when thus separated from the carbonate of magnesia, on evaporation to the consistence of a syrup, yielded *perfect*, *transparent* and *colourless*

* Chem. Gaz., vol. iii. p. 456. † Chem. Gaz., vol. i. p. 427.

crystals of milk-sugar. Hence it is certain that during the course of the first analysis the sugar had undergone a change; that probably at the long-continued temperature of 212° it had become converted by the free acid (phosphoric) present into grape-sugar, and as such remained with the extractives in a syrupy form.

In the milk of the same dog, examined after continuing diet of flesh for 12 and 27 days, crystals of sugar of milk were also found in both cases. In the case of the second dog, after 5 days' animal diet, the alcoholic solution reduced the oxide of copper with potash, although it did not yield crystals of sugar.

The author considers that the acidity of the milk arises from the presence of acid phosphate of lime, which salt, with the phosphate of magnesia, constitutes the greater part of the ash of this fluid. He thinks it probable, as previously stated, that the inability to procure milk-sugar from the milk of dogs fed exclusively upon animal diet arises from its conversion into grape-sugar by the acid phosphate of lime; whilst in the milk of dogs fed upon vegetable food, which has a neutral or alkaline reaction, this conversion is prevented.

It is evident from the above experiments, that even on long-continued exclusively animal diet the sugar does not disappear from the milk; hence the organism must possess the power of forming sugar of milk from the fatty or nitrogenous matters.—Liebig's *Annalen*, Bd. lxi. Heft 2.

Occurrence of Arsenic in Vinegar.

M. Deschamps found, on preparing pure acetic acid from wood-vinegar, that the latter contained arsenic, which he ascribes to arseniferous sulphuric acid having been used in the manufacture of the pyroligneous acid. As wine-vinegar is frequently strengthened with pyroligneous acid, M. Chevalier was induced to examine several samples of ordinary vinegar, and found some of them to contain very perceptible quantities of arsenic.—*Journ. de Chim. Méd.*, ii. p. 334.

On the Action of a Mixture of Sulphuric and Nitric Acids upon some Organic Substances. By A. Cahours.

The curious experiments of Pelouze upon pyroxyline, obtained by the action of a mixture of sulphuric and fuming nitric acid upon ligneous substances, as also the easy production of the binitrite of benzene, observed by Hofmann by means of a similar mixture, have induced me to submit to the same treatment the salycilate of methylene and salycilic acid, as well as several combinations belonging to the benzoic, anisic, cuminic series, &c., in the hope of giving rise to new compounds; my expectations have not been deceived, as will be seen from the following:—

When salycilate of methylene is poured drop by drop into a mixture formed of equal parts by weight of Nordhausen sulphuric acid and fuming nitric acid, taking care to cool the vessel containing the mixture by a stream of cold water, a perfectly transparent orange

liquid is obtained. On diluting the acid liquid with from 8 to 10 times its volume of water, a bright yellow heavy substance separates, which is almost insoluble even in boiling water, but dissolves in alcohol and æther, from which it separates in white crystalline laminæ with a slight yellowish tint. This product gave on analysis numbers leading to the formula $C^{16} H^6 O^6 + (NO^4)^2$. It is therefore salycilate of methylene, in which 2 equivs. hydrogen are replaced by 2 equivs. of hyponitric vapour. When the action is continued for a long time, a second product is obtained, which may be represented by the formula $C^{16} H^5 O^6 + (NO^4)^3$. Both these products, when treated with potash, are decomposed into a substance isomeric with picric acid, but from which it entirely differs in all its properties.

As anisic acid exhibits a perfect isomerism with the salycilate of methylene, I investigated the action which the sulphuronitric mixture would exert upon it. I had previously obtained, by means of nitric acid only, nitroanisic acid, which is isomeric with the indigotate of methylene; with the sulphuronitric mixture a trinitroanisic acid is produced, $C^{16} H^5 O^6 + (NO^4)^3$, which is isomeric with the trinitrosalycilate of methylene, and forms with alkaline bases, and especially with potash and ammonia, salts of great beauty.

On treating benzoic acid at a gentle heat with a mixture of sulphuric and nitric acids, I obtained a perfectly crystalline substance, which on analysis yielded the formula $C^{14} H^4 O^4 + (NO^4)^2$ It is therefore binitrobenzoic acid.

Cuminic acid, treated with fuming nitric acid, exchanges 1 equiv. hydrogen for 1 equiv. hyponitric vapour, and yields nitrocuminic acid $= C^{20} H^{11} O^4 + NO^4$. If the sulphuronitric mixture be employed instead of the nitric acid alone, cuminic acid parts with 2 equivs. of hydrogen, and takes up 2 equivs. of nitrous vapour, yielding binotrocuminic acid $= C^{20} H^{10} O^4 + (NO^4)^2$.

Salycilic acid, when treated with the sulphuronitric mixture, yields at first indigotic (nitrosalysilic) acid if care is taken to cool well; but if the temperature is raised, a violent reaction ensues, and the final product is carbazotic (nitrophenisic) acid. In this conversion of indigotic into carbazotic acid, carbonic acid is disengaged. If, instead of employing nitric acid alone, the sulphuronitric mixture is used, M. Deville's benzoine, $C^{14} H^8$, may be converted in a few minutes into binitrobenzoine $= C^{14} H^6 + (NO^4)^2$, which this chemist had previously obtained by using a large excess of nitric acid, and boiling for a considerable time.

When mesitylene is acted upon by the sulphuronitric mixture, it instantly yields, without any elevation of temperature, a crystalline substance, which sublimes at a gentle heat in the form of dazzling white delicate needles. The formula of this product is $C^6 H^3 + NO^4$. Mesitylene being represented by the formula $C^6 H^4$, it is seen that the preceding product is derived from it by the substitution of 1 equiv. hyponitric vapour for 1 equiv. hydrogen.

The mixture of sulphuric and nitric acids therefore acts upon the majority of organic substances, giving rise to definite compounds, which contain more hyponitric vapour than when nitric acid alone

is employed. In the various compounds which I have investigated, the introduction of a molecule of nitrogen was constantly accompanied by the elimination of a molecule of hydrogen. Now in what manner does the sulphuric acid act in this mixture? Is it by assimilating the water which the organic substance might otherwise retain? But the phænomena are the same whether we act upon ternary products containing water of crystallization or of combination, such as lignine, starch, sugar, dextrine, &c., or upon hydrocarbons like benzene, benzoine, naphthalene, &c. Is the nitrogen in the state of nitric acid, or as hyponitric vapour NO^4? It is, in my opinion, in the latter form in which it enters; at least in the case when hydrocarbons are acted upon, no other hypothesis is possible. In fact, on bringing nitric acid into contact with a hydrocarbon $C^m H^n$, we always obtain products derived from the form

$$C^m H^{n-1} NO^4,\ C^m H^{n-2} (NO^4)^2,\ C^m H^{n-3} (NO^4)^3,\ \&c.$$

Now

Nitrobenzene	$C^{12} H^5 NO^4$
Nitrobenzoine	$C^{14} H^5 NO^4$
Nitronaphthalene	$C^{20} H^7 NO^4$
&c.	&c.

can evidently not contain nitric acid NO^5; but if, in the reaction of the nitric acid upon the organic substance, the molecule NO^4 is substituted for a molecule of hydrogen, there is necessarily formation of water; thus $C^m H^n + NO^5 = C^m H^{n-1} NO^4 + HO$. This water, which results from the action of the acid upon the organic substance + that which is derived from the portion of acid decomposed, is consequently added to that of the remaining nitric acid, and tends to weaken it. Does not the concentrated sulphuric acid in this mixture serve to retain this water, so that, preventing the hydration of the unemployed nitric acid, it enables this to react in its turn upon the product first formed, and thus to give birth to a new substance, derived by substitution?

I may add, in conclusion, that cumene, treated with fuming nitric acid, yields nitrocumene, and binitrocumene when acted upon with a mixture of sulphuric and nitric acids. By acting upon these two products with hydrosulphate of ammonia, I have obtained two new alkaloids, *cumine* and *nitrocumine*, which form readily crystallizable salts with acids.—*Comptes Rendus*, March 29, 1847.

ANALYTICAL CHEMISTRY.

On the Estimation of Sulphur in Organic Substances.
By H. Weidenbusch.

The method of determining sulphur by burning the substance with nitre and caustic potash is, as regards accuracy of the results, perfect, but its execution is difficult and tedious, and renders a more simple method desirable. In the first place, it is not very easy to procure caustic potash perfectly free from sulphur; further, the

decomposition of the substance is very often accompanied by a loss, owing to portions being projected; and lastly, the silver vessel is each time so violently attacked, that the mass obtained after combustion on saturation with muriatic acid always deposited a precipitate of chloride of silver. I was therefore induced by Prof. Liebig to try again strong nitric acid conjointly with nitrate of baryta. The substance was mixed with an excess of this salt, and stirred in a beaker glass with the most concentrated fuming nitric acid to a thin paste; the mixture was exposed in a covered beaker to the temperature of the sand-bath, replacing the evaporated nitric acid until the organic substance was entirely destroyed, which is perceptible from the circumstance that on evaporating the nitric acid still present, the mass begins to thicken, but no longer ascends in large bubbles in the glass, and dries quietly without frothing. The decomposed mass is now carefully washed into a platinum dish, dried at 212°, and then heated gradually until the saline mass is perfectly liquid. If the organic substance had not been entirely destroyed by the nitric acid, it frequently happens that the mass takes fire, and a portion is projected from the slight deflagration. This must be avoided, as it occasions a loss of substance; but even though this were not the case, a smaller quantity of sulphate of baryta is obtained, according to my observations; for it appears as if the sulphur still contained in organic combination is not oxidized so readily by the deflagration of the mass as by the slow action of the nitric acid. The fused mass is carefully separated from the platinum dish and treated in a beaker glass with dilute acetic acid, and heat applied as long as any evolution of gas is perceptible. The carbonate of baryta is decomposed, and the residue consists of pure sulphate, which is collected on a filter, washed, dried, heated to redness, again digested with acetic acid after ignition, and again heated to redness. After the second ignition it is perfectly pure, and the amount of sulphur may be calculated from it. This method has proved perfectly trustworthy in numerous experiments, which for comparison's sake were made according to both plans; for instance, the sulphur determinations of fibrine gave absolutely the same numbers as those published by Verdeil*.

It appears that the simultaneous addition of the barytic salt to the nitric acid acts an essential part, and that the presence of the baryta, which possesses so powerful an affinity for sulphuric acid, renders the oxidation of the sulphur more easy and perfect.—Liebig's *Annalen* for March.

Remarks on the application of Liebig's new Test for Prussic Acid to Medical Jurisprudence. By Alfred S. Taylor, *F.R.S.*

Professor Liebig's test has been detailed in the complete translation of his original paper at page 143 of the present volume of this journal. The following remarks illustrate the great delicacy of this

* See Chem. Gaz., vol. iv. p. 363.

valuable test so clearly, and point out many precautions which render its applicability to medical jurisprudence so very satisfactory, that we have abstracted it almost completely.

The prussic acid employed in the following experiments was first accurately examined as to its strength. Two hundred grains gave by precipitation with nitrate of silver 14·3 grains of dry cyanide of silver. This would be equal to 2·88 grains of anhydrous prussic acid, or 1·44 grain per cent.

Prussic acid.—Two drops of this acid (=·028 gr., or about 1-36th of a grain of anhydrous acid) were placed in a watch-glass and heated with a drop of the common hydrosulphuret of ammonia. When the liquid had entirely lost its yellow colour, an opake film appeared on the glass; and, on adding one drop of a solution of persulphate of iron, an intense *blood-red colour* was immediately produced. The colour was entirely destroyed, and the liquid became colourless, on the addition of two or three drops of a solution of bichloride of mercury. It was thus evident that the prussic acid and hydrosulphuret of ammonia had reacted upon each other, producing sulphocyanate of ammonia and a thin film of sulphur, which might have been easily separated by water, but it did not in the least degree interfere with the chemical reaction upon which the operation of the test depended.

Chemical changes.—The common hydrosulphuret of ammonia employed (NH^3 HS, or NH^4 S, + HS) was of a yellow colour; the ammonium was therefore most probably in the state of bisulphuret (NH^4, S^2), one equivalent of hydrogen having combined with the oxygen of the air. Admitting this to be the composition of the hydrosulphuret, although ammonium has, like potassium, several degrees of sulphuration, the chemical reaction may be explained by the following formula:—

$$NH^4,S^2 + H,Cy + O = NH^3,CSy + HO \text{ or } NH^3,CyS^2H + HO.$$

The slight residue of sulphur may have been owing to the hydrosulphuret being in excess, compared with the quantity of prussic acid present. From the substances employed, and the results, it is evident that if the boiling and evaporation be not carried far enough, the persalt of iron will be precipitated by the undecomposed hydrosulphuret of ammonia; and, if the heat be carried too far, the sulphocyanate of ammonia may itself undergo decomposition.

Diluted Prussic acid.—The prussic acid employed in the previous experiment was now much diluted with water. Two drops of the acid were thoroughly diffused in 220 grains of distilled water; and each grain of this mixture would therefore contain no more than 1-7860th (220÷·028) of a grain of anhydrous acid.

In order to compare the effect of the new with the old tests, ten minims of this very diluted acid were tried with the common prussian blue test. The liquid acquired a yellowish tint; but after several hours there was no perceptible deposit of prussian blue. Thus the iron test failed entirely to detect the 1-786th of a grain of prussic acid in ten minims of water. It required one drachm and a half

of this diluted acid (=1-87th grain) to produce after twenty minutes a perceptible deposit of a prussian blue of a greenish colour. A like quantity (ten minims) was taken, and a solution of nitrate of silver added to it. There was only a faint opalescence, but no deposit of cyanide of silver. The silver test therefore failed in detecting the 1-785th of a grain of the acid; for the production of a faint opalescence could not be regarded as indicative of the presence of the poison. The effect of this test became apparent with one drachm of the diluted acid (=1-131st part of a grain), but still there was no visible deposit of cyanide of silver.

It need hardly be remarked that in this highly diluted condition there was not the least perceptible *odour* of the poison *.

Two minims of the diluted acid were now placed in a watch-glass with one minim of diluted hydrosulphuret of ammonia, and gently evaporated to dryness. A drop of the persulphate of iron added to the residue gave immediately a reddish tint indicative of the presence of sulphocyanic acid or a sulphocyanate. The quantity of anhydrous acid which was here clearly detected by the test was not more than 1-3930th of a grain! (7860÷2.) It was evident therefore from these results, that Prof. Liebig had not exaggerated the delicacy of this valuable test. It is capable of indicating the presence of prussic acid when no odour can be perceived, and when the iron and silver tests fail to act with any degree of certainty.

The reader will perceive that the cause of this highly-delicate reaction is, that we obtain the residue in a solid, and therefore in a most concentrated state. There is no water to dilute or destroy the intense blood-red colour characteristic of the sulphocyanate of iron. Hence the chemical changes are most perfectly brought out on the smallest visible quantity of residue. The only precaution required is, not to add too much of the persulphate of iron; a fractional part of a drop will commonly suffice. The salt of iron should be used in a concentrated state, and as neutral as possible.

The application of Prof. Liebig's process, however, presupposes that the experimentalist has the prussic acid in a free and pure condition. In medico-legal practice, the poison, as we know, is liable to be mixed up with mucus, blood, articles of food, and other matters. It would be impossible to employ the test under these circumstances. It would always be necessary to distil the contents of the stomach or vomited matters; and from the numerous objections which have been taken to medical evidence, it is decidedly advisable to avoid the process of distillation, until *after* the poison has been clearly detected without it. It may then be required, not to determine the presence of prussic acid, but the *quantity* contained in the suspected liquid. Further, supposing the contents of the stomach

* I have elsewhere shown, with respect to the action of nitrate of silver on a solution of prussic acid, that it will produce a milkiness with the 4000th of a grain of anhydrous acid in a minimum of water; but it only begins to give a decided precipitate with the 220th of a grain in about 13,000 parts of water.—*Guy's Hospital Reports*, April 1845.

to be in a decomposed state, or to contain hydrosulphuret of ammonia, a body which I have on several occasions found in them, it is clear from the foregoing experiments that the application of heat would cause any prussic acid to react upon the sulphur compounds, and to form a fixed sulphocyanate, so that none of the poison might pass over into the receiver.

In a paper published in this journal * in June 1845, I suggested a plan for detecting prussic acid without distillation, by taking advantage of its great volatility, and the action of its vapour on a solution of nitrate of silver. The experiments there related, as well as those performed by Mr. Hicks †, show that this is a most delicate mode of testing, and that it is open to no practical objection ‡. I have found, however, in testing putrescent liquids, and animal matter containing prussic acid, that the nitrate is darkened by the sulphur; and the reaction of the hydrocyanic acid is no longer clear or certain. This mode of employing nitrate of silver led me to the trial of a similar plan for the detection of prussic acid by the hydrosulphuret of ammonia.

Modification of the test.—Place the diluted prussic acid in a watch-glass, and invert over it another watch-glass, holding in its centre one drop of the hydrosulphuret of ammonia. There is no apparent change in the hydrosulphuret; but if the watch-glass be removed after the lapse of from half a minute to ten minutes, according to the quantity of prussic acid present, sulphocyanate of ammonia will be obtained on gently heating the drop of hydrosulphuret and evaporating it to dryness. The addition of persulphate of iron to the dried residue brings out the blood-red colour instantly, which is intense in proportion to the quantity of sulphocyanate present. Such is the simple method of employing the test: it is wholly independent of distillation and (unless the prussic acid be excessively diluted) of any application of heat. In this case the warmth of the hand may be required to expedite the evolution of the vapour.

Whatever proportion of acid may be detected by the mixture of the two liquids, as suggested by Prof. Liebig, may be with equal certainty discovered by this process. Thus two drops of the highly-diluted acid just now mentioned, gave, after a few minutes' exposure to the hydrosulphuret, a clear reaction; while it was found that a drop of solution of nitrate of silver placed in a watch-glass and inverted over that containing the diluted acid, gave no opake film (cyanide of silver) until after the lapse of half an hour! Hence the process is even more delicate than that of the reception of the vapour on a solution of nitrate of silver, as suggested in a former communication to this journal §.

* Medical Gazette, vol. xxxvi. p. 328. † Ibid. page 631.

‡ Although the vapours of muriatic acid, when in a certain strength (never found naturally in the body), produce also a white film on a solution of nitrate of silver, I have since found that these are easily known from those caused by prussic acid, by the rapid darkening under exposure to light. The thin film of cyanide is soluble in an excess of strong nitric acid—that of the chloride is not.

§ Medical Gazette, vol. xxxvi. p. 328.

The two tests may be usefully employed together. If a suspected liquid, placed in a watch-glass, produce a film on a drop of nitrate of silver, the reaction will be very speedy with the hydrosulphuret. The silver test acts *visibly*, and therefore serves to guide us: the hydrosulphuret acts invisibly; for there is no apparent change unless the glass be left so long that the ammonia is spontaneously evaporated, and the sulphur oxidated or deposited. If the suspected liquid produce, after half an hour, no effect by its vapour on a drop of nitrate of silver, it is very probable that no prussic acid is present: nevertheless, we should proceed to apply the hydrosulphuret of ammonia, as I have found the poison by it when nitrate of silver had entirely failed to indicate its presence.

Rapidity of action.—Twenty drops of prussic acid, so diluted as to have a strength in anhydrous acid of only 0·48 per cent., therefore rather less than one-fourth the strength of the London Pharmacopœial acid, were placed in a watch-glass. On inverting over it another watch-glass containing a drop of nitrate of silver, it was whitened immediately; a drop of hydrosulphuret of ammonia was then substituted. By two separate trials, sulphocyanate was found to have been formed in *ten seconds*, and the effect was very strong in thirty seconds; the quantity of anhydrous prussic acid here detected was ·096 gr., or about 1-12th of a grain. It would be in general advisable to expose the hydrosulphuret to the vapour for one or two minutes, and when the acid is very diluted, for from ten minutes to half an hour. The following experiment will, however, show that the absorption is extremely rapid, even when the acid is much diluted. Three drops of the prussic acid above employed were diffused through two drachms of distilled water; no odour whatever could be perceived in this mixture; ten drops were placed in a watch-glass, and nitrate of silver was speedily whitened by the vapour. The effect with hydrosulphuret of ammonia was distinctly procured in five minutes; the total quantity of anhydrous acid present in the ten drops of liquid did not exceed the 1-473rd part of a grain!

Laurel water.—A very weak specimen of laurel water was next examined. Nitrate of silver produced no perceptible effect with one drachm of it when the liquids were mixed, nor could any prussian blue be procured from a like quantity by the use of the iron test. One drop of hydrosulphuret of ammonia, added to three drops of the water, gave the clearest evidence of prussic acid by the production of the red sulphocyanate of iron, when the persulphate was added to the evaporated residue. From five to ten drops, placed in a watch-glass, produced no film (by the vapour) on nitrate of silver after the lapse of twenty minutes: in the same period of time, one drop of hydrosulphuret of ammonia absorbed the vapour, and left, on evaporation, a perceptible quantity of sulphocyanate.

Bitter Almond water.—Two specimens of this water, prepared by the distillation of bruised bitter almonds with water, were tried merely by volatility, as it was certain that if this experiment succeeded, the mixture of liquids could not possibly fail. With one specimen, after half an hour, no effect had been produced on nitrate

of silver; and on trying the hydrosulphuret, no sulphocyanate of ammonia was detected in the evaporated residue. Two drachms of this water gave no perceptible precipitate with nitrate of silver, nor could any prussian blue be obtained by adding the iron test to a similar quantity of liquid. The second specimen of bitter almond water, which was slightly precipitated by nitrate of silver, and affected that liquid by its volatility, gave decided evidence of prussic acid in *three minutes* by the hydrosulphuret of ammonia.

Bitter Almonds.—It is not easy to detect the prussic acid evolved by the admixture of water in the pulp of *one* bitter almond; the iron test gives, however, a blue deposit (prussian blue) after some hours. The pulp obtained from *one half* of a bitter almond, bruised with water, faintly affected nitrate of silver by its volatility, but in a quarter of an hour gave clear evidence of prussic acid with the hydrosulphuret of ammonia.

Essential Oil of Bitter Almonds.—The vapour of this oil, if long kept, only faintly affects nitrate of silver by its volatility; and does not readily give a precipitate of cyanide of silver on the addition of this test; *one drop* of the oil gave, in a few minutes, distinct evidence of prussic acid, in absorbing its vapour by hydrosulphuret of ammonia.

Decomposed Prussic Acid.—This was a specimen which had been kept three years; it was quite blackened, and in a thick and syrupy condition; it produced by its volatility an opake film in a few seconds, and the prussic acid, still remaining in it, was detected in an equally short period by the hydrosulphuret.

Hydrocyanate of Ammonia.—The combination of prussic acid with alkaline bases does not prevent this delicate reaction. To one drop of the acid employed, two drops of a moderately strong solution of ammonia were added: the liquid was strongly alkaline. Nitrate of silver was rendered opake by its vapour, and the hydrosulphuret gave the usual evidence of the acid in a few minutes. When a very large excess of strong solution of ammonia was added, there was no effect on exposing to the vapour the nitrate of silver or the hydrosulphuret; but by diluting the liquid, and then acidulating it with diluted sulphuric acid, satisfactory results were obtained with both tests in a few minutes.

Cyanide of Potassium.—A single grain of this salt moistened with water, forming a strong alkaline solution, gave by its vapour a well-marked action on the silver and hydrosulphuret in a few seconds. An alkali, therefore, does not fix the acid so as to prevent the action of the tests. This is important in examining decomposed organic liquids, or those into which we do not wish to introduce an acid.

Cyanides of Silver and Mercury.—Half a grain of each of these salts moistened with strong muriatic acid gave characteristic reactions with both tests in a few seconds. Any visible quantity of either cyanide in small glasses would suffice to give evidence. This is an excellent and easily-applied experiment for determining the nature of a precipitate supposed to be cyanide of silver, when a sufficient quantity cannot be obtained for the combustion of cyanogen,

and we are unwilling to trust to odour alone. While it is much more easily applied than that suggested by Dr. Austin, of heating the precipitate with iron and potassium, the results are just as satisfactory. Prussian blue, not being easily decomposed by muriatic acid, produced no effect with the tests. This compound might, if required, be examined by digestion in potash, pouring off the ferrocyanide of potassium, and adding sulphuric acid.

Ferrocyanide of Potassium.—A grain of this salt in powder mixed with water and strong sulphuric acid, on the application of a moderate heat, yielded a vapour which affected the silver and the hydrosulphuret in two or three minutes. The last experiments resorted to were perhaps the most important in a medico-legal point of view.

In decomposed organic liquids.—The putrefied contents of the stomach of a female who had died under a suspicion of irritant poisoning about three weeks before, were taken for the first experiment. The odour was highly offensive,—acetate of lead was immediately blackened by the vapour, and the trial test of silver was also blackened by the sulphur: consequently in this case it could not be used for the detection of prussic acid. To *one drachm* of this offensive liquid *one drop* of the acid employed (=·014 or 1-71 of a grain of anhydrous prussic acid) was added, and a watch-glass, with hydrosulphuret of ammonia, was placed over it. In a few minutes the presence of prussic acid was most satisfactorily detected.

To an equal portion of decomposed vomited matter, consisting of blood, mucus, bile, and other substances, *one drop* of the acid was added; and when the hydrosulphuret was exposed to the vapour, the results obtained were equally satisfactory. Nitrate of silver could not be employed in this case, as it was immediately blackened by the vapour.

It will thus be seen that the process is more delicate, more speedily and universally applicable, and more certain and unobjectionable in its results, than any of those yet suggested for the detection of this powerful poison. To Prof. Liebig belongs the merit of this discovery, and by announcing it he has placed in the hands of chemists a means of tracing crime in cases in which our present resources would have entirely failed us. He has here done for prussic acid what Reinsch has recently done for arsenic: the analysis may be made during the post-mortem examination of a body, and the result relied on as conclusive both affirmatively and negatively.

Objections.—I am not aware of any objections to this process for detecting prussic acid when we absorb the vapour of the acid, previously to distillation, by hydrosulphuret of ammonia. There must be some compound of cyanogen capable of uniting with sulphur to form sulphocyanic acid, and capable of being evolved from a body at common temperatures in a few seconds in order to produce the effects described; and, so far as I am aware, no such body exists. If it did, and these results were obtained, they would still furnish a proof of its containing a powerful poison—cyanogen. I have not had an opportunity of trying the bromide and iodide of cyanogen; but these compounds are well-characterized by other properties, and

are not likely to be confounded with hydrocyanic acid. The preliminary test of nitrate of silver will besides aid us in many cases which might present some apparently ambiguous results. The sulphocyanic acid exists in the saliva, but as it is combined with a base, it cannot be volatilized at common temperatures so as to mix with the hydrosulphuret, and lead to deception. As white mustard contains a principle (sulphosinapisin) capable of being converted to sulphocyanic acid, a quantity of the seed was bruised, placed in a watch-glass, and exposed to hydrosulphuret of ammonia. The pulp immediately acquired a yellowish tint from the vapour of the ammonia, but after a quarter of an hour's exposure to the hydrosulphuret, it left no sulphocyanate on evaporation. On pouring some persulphate of iron on the pulp, it acquired a dingy red colour.

The proof, therefore, of the presence of prussic acid by this process is based on two facts; 1st, the great *volatility* of a cyanogen compound in a state fitted to combine with sulphur to form sulphocyanic acid; and 2nd, the production of an intense *red colour* with a persalt of iron capable of being entirely destroyed by a few drops of bichloride of mercury. I believe that there is no substance known to chemists which fulfils these conditions except prussic acid: hence no other test is required for the poison. The prussian blue test may be occasionally employed as corroborative, and I have found that a useful method of applying it is to precipitate the mixed oxides from the green sulphate in a gelatinous form, and to expose them to the vapour of the acid in a watch-glass.

It must be understood that the new test merely demonstrates the *presence* of the poison. For a quantitative analysis, distillation and the use of the nitrate of silver must still be resorted to. If distillation be employed qualitatively, a small quantity of hydrosulphuret of ammonia might be placed in the receiver in order to fix the vapour when the quantity of poison was small.

It may be proper to state, that if the hydrosulphuret of ammonia have absorbed no prussic acid, it gives before evaporation a black precipitate with persulphate of iron; if it be evaporated until the yellow colour has disappeared, should no sulphocyanate be present there is merely a yellow tint from the separation of sulphur. Other alkaline sulphurets may be substituted for the hydrosulphuret of ammonia, but they must be always in the state of polysulphuret: and the chemical reaction with prussic acid is never perfect until after heat has been applied to the mixed liquids or to the sulphuret which has absorbed the vapour.—*From the 'Medical Gazette' for April* 30, 1847.

CHEMICAL PREPARATIONS.

Experiments on Carotine. By W. C. Zeise.

The peculiar substance contained in the root of *Daucus carota* was hitherto unknown in the pure state; for by the process usually employed to extract it, viz. treating the coagulated juice

with æther, evaporating, and treating the residue with alcohol or ammonia, the carotine obtained is always combined with a large quantity of fatty oil, and the product forms a soft mass containing crystals of carotine; the author tried several processes to obtain it pure, and at last succeeded by the following:—The roots are submitted to pressure, the juice diluted with from 4 to 5 vols. of water, and to the mixture sulphuric acid diluted with 10 vols. of water added. Even a very small quantity of this acid precipitates the whole of the colouring matter of the juice. The liquid is decanted, and the mass thus obtained washed with water, after which it is boiled for an hour or an hour and a half with a tolerably strong solution of caustic potash. The potash saponifies the fatty oil, and dissolves a trace of albumen, but does not act upon the carotine, which is collected on a filter and washed with water. In this state it still contains a saline body, which must be decomposed in order to prevent it accompanying the carotine in the following operation; for which purpose the mass is suspended in water and heated, and an excess of dilute sulphuric acid added to it. After having again collected the carotine upon a filter and well-washed, it is treated at first with dilute, and finally with nearly anhydrous alcohol, in order to separate the fatty acid; but very little carotine is dissolved in this operation. The mass is then dried in the water-bath.

When freed from oil, carotine dissolves very sparingly in æther; but to complete its purification, M. Zeise turned to account a property of carotine which he had occasion to observe, that of being extremely soluble in sulphuret of carbon. The well-dried mass is therefore treated with this agent, and the dark red solution separated from a grayish substance, which remains undissolved. After having distilled off nearly three-fourths of the sulphuret of carbon, anhydrous alcohol is added to the residue; when, on leaving the mixture in an open dish, the carotine soon separates in the form of very minute deep red crystals. The mother-ley is decanted, and the crystals washed on a filter with anhydrous alcohol until this passes off nearly colourless; the carotine is now perfectly pure. In appearance it has some resemblance to coarsely-powdered vermilion, or to copper reduced from the oxide by hydrogen. The crystals are very minute, and possess a highly metallic lustre.

Carotine has a very faint, rather pleasant odour; it is heavier than water, and is entirely insoluble in it; nearly insoluble in alcohol and in pyroligneous æther, when this is perfectly free from oil, and very slightly soluble in æther and in acetone. It melts at 334° F. into a perfectly transparent dark red liquid, and solidifies on cooling to a vitreous mass. After having been melted, it dissolves readily in æther and in alcohol; but these solutions on evaporation furnish only an amorphous mass. It chars at 549°, yielding a small quantity of an oily body and very little gas; when heated in the air, it burns with flame, and leaves not a trace of residue. From the elementary analysis of this body, it results that it is a combination of carbon and hydrogen in the atomic proportion $10(C^5 H^8)$; carotine

is consequently polymeric with oil of turpentine, a fact of considerable interest.

Dry chlorine has no action upon dry carotine, but it is converted into a perfectly colourless chlorinated body by water saturated with chlorine; this substance is insoluble in water, but dissolves in alcohol, æther, and in sulphuret of carbon. The solutions yield on evaporation a brittle resinous mass.—*Ann. de Chim. et de Phys.*, May 1847.

On the Preparation of Ferrideyanide of Potassium.
By A. *and* C. Walter.

Yellow prussiate of potash is boiled with 12 to 15 parts of water, and while boiling good chloride of lime added until a filtered sample appears red, or no longer yields a blue precipitate with persalts of iron. It is then quickly filtered, a little carbonate of potash added to the solution until it has a faintly alkaline reaction, and then evaporated to crystallization; the crystals obtained are purified by recrystallization.—Buchn. *Rep.*, xliv. p. 42.

On the Preparation of pure Metallic Antimony.
By Dr. C. G. Wittstein.

The process proposed by Liebig for the preparation of pure antimony is not capable, according to the observations of several persons, of removing every trace of arsenic, however often the fusion be repeated; it is also quite impossible to get rid of the lead by this method. The best mode of preparing the pure metal is to reduce the oxide by charcoal, as already proposed by Artus. The oxide is best obtained by dissolving in a large flask 2 parts of sulphuret of antimony in 8 parts of crude muriatic acid, warming until the whole of the sulphuret of hydrogen is expelled, and then adding 1 part of crude nitric acid of 1·2 spec. grav. When no further nitrous vapours are perceptible, the liquid is mixed with so much water (about 4 parts) that it does not become turbid, filtered after settling through a double filter, the solution precipitated by a large quantity of water, and the precipitate washed until the water which passes off is no longer acid; it is then digested in the pasty state with one-third part of crystallized carbonate of soda, and after washing dried. To reduce the pure oxide of antimony thus prepared, it is rubbed to a fine powder, mixed with one-eighth its weight of finely pulverized charcoal, the mixture pressed firmly into a crucible covered with a layer 2 inches in depth of common salt, and slowly heated to redness, now and then pressing the mass, which cakes together, into the crucible. If, on breaking through the layer of muriate of soda the metal beneath is found to be fluid, the opening made is immediately stopped with common salt, a red heat continued for a quarter of an hour, and then the whole allowed to cool. The slag of chloride of sodium is first removed, and the crucible, together with its contents, boiled with water to obtain the metallic granules still contained in the slag. As the volume of the oxide of antimony is very great, it

is requisite to employ large crucibles. The author never obtained more than 11 oz. of pure metal from $18\frac{2}{3}$ oz. of crude sulphuret of antimony, which according to theory should yield $13\frac{1}{2}$ oz. The loss is owing to the impurity of the raw material, waste in filtering and precipitating, and to the volatility of the metal. The expense is by no means greater than according to Liebig's process.—Buchn. *Rep.*, xliv. p. 45 to 57.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 5, 1847. (Thomas Graham, Esq., Vice-President, in the Chair.)

"On Decompositions produced by Catalytic Bodies," by Lyon Playfair, Ph.D.

After reviewing the theories on catalytic decomposition by Berzelius and Liebig, the author preferred the view originally proposed by Mercer, which ascribed such changes to the action of a feeble chemical affinity. Numerous examples were cited in proof of the latter view, such as the oxidizing power of chloride of manganese or nitrous acid on a mixture of organic matter; the spontaneous inflammability given to non-inflammable phosphuretted hydrogen by NO^4; the decomposition of HO^2 by the oxides, &c.

Catalysis was defined to be the chemical affinity of a second body acting in the same direction as the affinity of the first body which suffers changes. The nature of the catalysis is owing to an inaptitude to enter into combination under the circumstances. The same explanation was applied by the author to certain phænomena, where he conceived opposite affinities to balance and prevent the play which might have been expected, as for instance the action of corrosive sublimate as an antiseptic, the affinity of the chlorine exerting as strong an attraction for the hydrogen of the decaying substance as the oxygen of the air does for the same element. The retarding action of carbonic oxide, olefiant gas, &c. in preventing the peculiar action of platinum on oxygen and hydrogen was similarly viewed. The action of yeast on sugar in causing it to pass into alcohol was considered by the author to come within the class of decompositions produced by a feeble chemical affinity. The paper also included some speculations on the molecular constitution of salts, which this view of catalysis seemed to point to as being preferable to the theory of acid radicals.

"Analysis of the Ashes of the Orange Tree (*Citrus aurantium*)," by Messrs. Thomas H. Rowney and Henry How.

The materials employed in this examination were supplied by M. da Camara of the island of St. Michels. After describing the methods of preparing the ash and the routine of analysis, the authors sum up with the following results:—

	Root.	Stem.	Leaves.	Fruit.	Seed.
Per-centage of ash	4·48	2·74	13·73	3·74	3·30
Potash	15·43	11·69	16·51	36·42	40·28
Soda.....	4·52	3·07	1·68	11·42	0·92
Lime	49·89	55·13	56·38	24·52	18·97
Magnesia.....	6·91	6·34	5·72	8·06	8·74
Oxide of iron	1·02	0·57	0·52	0·46	0·80
Chloride of sodium....	1·18	0·25	6·66	3·87	0·82
Phosphoric acid	13·47	17·09	3·27	11·07	23·24
Sulphuric acid.....	5·78	4·64	4·43	3·74	5·10
Silicic acid	1·75	1·22	4·83	0·44	1·13
	100·00	100·00	100·00	100·00	100·00

These results confirm the observations of Saussure, that the largest amount of mineral constituents is deposited in those parts of the plant in which the process of assimilation appears to be most active. In the ashes of the root, the stem and the leaves, the joint amount of the lime and magnesia exceeds the rest of the mineral constituents. In the fruit and seed the alkalies are prevalent.

Mr. Warren De la Rue described and exhibited an improved form of Will and Varrentrapp's nitrogen apparatus, which he had used for the last 18 months past, and by which the liability of the hydrochloric acid to be drawn into the combustion-tube from the sudden absorption of the ammoniacal gas is obviated.

"On the Chemical Constitution of Metacetonic Acid, and some other Bodies related to it," by E. Frankland and Dr. H. Kolbe.

The idea recently started, that certain organic acids might be looked upon as conjugate compounds containing an acid of simpler constitution united to a second body without diminution of its capacity of saturation, led the authors to undertake certain experiments in the above direction. The possible conversion of cyanide of ethyle into metacetonic acid and ammonia first engaged their attention.

Pure cyanide of ethyle was prepared by the process of Pelouze, by distilling together sulphovinate of potash and cyanide of potassium, washing the product with water, and finally distilling it from chloride of calcium in a tube-retort void of air. Its purity was proved by analysis. The cyanide of ethyle was then added drop by drop to a tolerably concentrated boiling solution of caustic potash, and the distilled product returned to the retort as long as it retained any smell. During this operation much ammonia was given off. The alkaline residue distilled with sulphuric acid produced an acid liquid having all the characters of metacetonic acid. The salts of silver, lead and baryta were formed and examined by analysis, and all doubt of the nature of the acid set at rest.

Cyanide of ethyle is also decomposed by dilute sulphuric acid, with formation of the same product.

April 19, 1847. (The President, Professor Brande, in the Chair.) The following papers were read:—

"On the Decomposition of Valerianic Acid by the Voltaic Current," by Dr. H. Kolbe.

The author finds that when valerianate of potash is subjected to the action of the voltaic current, it is resolved into hydrogen, carbonic acid, a new gaseous hydrocarbon, and an oily body having an æthereal odour, together with carbonate and bicarbonate of potash. The æthereal oil consists of two compounds, one of which is free from oxygen, and is composed of $C^8 H^9$; the other Dr. Kolbe considers as a compound of valerianic acid with the oxide of this hydrocarbon. The gaseous hydrocarbon $C^8 H^8$ has a peculiar æthereal smell, a specific gravity double that of olefiant gas, and unites with chlorine even in the dark to form a heavy oily liquid similar to chlorelayle. Butyric and acetic acids are acted on in a similar way; the products from acetic acid are all gaseous; butyric acid yields in addition a volatile oil, $C^6 H^7$. Dr. Kolbe considers that valerianic acid may be viewed as a conjugate compound of the radical $C^8 H^9$ with oxalic acid.

"An Account of Experiments with Voltaic Couples immersed in pure Water and in Oxygenated Water," by Mr. Richard Adie.

After alluding to some previous published experiments on this subject, the author states that, on examining after a lapse of two years an arrangement of voltaic couples placed in a tube and hermetically sealed, the tubes burst with violence, evidencing a true decomposition of water, although the metals were bright and the water transparent. The nature of the battery which had been sealed in the tube is then minutely described, and the precautions used to exclude atmospheric air. On examining the inner surface of the glass and the plates, they were found to be covered with minute crystals of protoxide of zinc. The effect of a zinc and copper couple in pure water on the galvanometer was then examined; and it was found that previous to boiling the needle stood at 50°; at the moment boiling was about to commence it indicated 70°, and after long boiling 20°, the greatest indication occurring at the time the water was parting with the dissolved air, proving that, in addition to the action of the water-battery being supported by the absorption of atmospheric air, there is a minute degree of action when it is excited by pure water. When two slips of the same metal are placed in a stream of water, the one being in a part of the fluid in rapid motion, the other in a quiescent part, and connecting these with a galvanometer, a permanent deflection of 25° was observed; and by changing their respective positions, without disturbing their attachments, the needles passed to the opposite side, the air contained in the water of the current converting it into a negative electrode. With both plates in still water, and a tube of oxygen over one of them, the effect was the same. Metallic precipitations were also effected by this arrangement. Iron plates produced the same effects; and the author considers that these experiments establish the existence of an electrolyte more easily decomposed than water and as universal in nature. A saturated solution of carbonate of potash or soda, in an open cylindrical vessel, so completely shuts out the atmospheric air, that pieces of iron have remained immersed two years and four months without any appearance of corrosion.

THE CHEMICAL GAZETTE.

No. CXII.—June 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Nitrosulphuric Acid, and its Behaviour towards Sulphur, Selenium, Phosphorus and Iodine. *By* Prof. SCHÖNBEIN.

If I am not mistaken, it is generally admitted by chemists that the monohydrated sulphuric acid may be mixed in the cold with the first hydrate of nitric acid, without the one in any way chemically acting upon the other. The theoretical views which I entertain on these hydrated acids led me to suspect that this assumption was erroneous. Starting on the supposition that the hydrate of sulphuric acid $= SO^2 + HO^2$, the hydrate of nitric acid $= NO^4 + HO^2$, and Rose's bisulphate of the oxide of nitrogen $= 2SO^2 + NO^4$, I considered it as probable that, on mixing the above hydrated acids, the last-mentioned compound would be formed, and consequently that the peroxide of hydrogen contained in the two acids would either be eliminated, or remain feebly combined with the sulphite of hyponitric acid, according to the equation

$$2(SO^2 + HO^2) + NO^4 + HO^2 = 2SO^2 + NO^4 + 3HO^2.$$

Adopting this view, it would result that the nitrosulphuric acid would oxidize far more powerfully than nitric and sulphuric acids in their isolated state; in other words, that this acid mixture would behave towards several bodies as a kind of *aqua regia*, in which the chlorine is replaced by peroxide of hydrogen. Another consequence of my hypothesis would be, that water would separate nitric oxide from the mixture, provided this were deprived of its HO^2 by an oxidizable body. The following statements will show in how far experiment agrees with the view advanced.

I. When flowers of sulphur are added to a mixture of the above hydrated acids, sulphurous acid is instantly given off. According to the proportion in which the two acids are mixed and the temperature of the mixture, the reaction with sulphur varies somewhat. When 2 oz. of pure oil of vitriol are mixed with only 1 drop of the hydrate of nitric acid, a perceptible quantity of sulphurous acid is disengaged even at 32° F., when the acid mixture is stirred with flowers of sulphur.

To render the presence of such minute quantities of sulphurous acid perceptible when they can no longer be detected by the smell,

I employ a strip of paper dipped into iodide of potassium paste, which has been previously rendered slightly blue by immersion in an atmosphere of chlorine. This blued paste is instantly decolorized by the merest trace of sulphurous acid*. A slip of paper dipped into tincture of guaiacum, and rendered slightly blue by chlorine, may be employed for the same purpose.

On shaking 1 grm. flowers of sulphur and 60 grms. of an acid mixture, formed of 9 parts oil of vitriol and 1 part of the first hydrate of nitric acid, sulphurous acid is immediately disengaged at a temperature of 32°; in the course of a few minutes the liquid froths violently, owing to the abundant evolution of sulphurous acid, and at the same time the acid mixture becomes very hot; but soon the frothing ceases, the liquid again cools, becoming brighter, the whole of the sulphur disappears, and the disengagement of sulphurous acid ceases entirely. During the whole of this reaction only sulphurous acid is disengaged; except the frothing is very violent, when it is mixed with traces of hyponitric acid. When the experiment is made in a tall glass, so that no loss can occur from the frothing, and the whole is weighed before and after the reaction, the loss is found to be exactly equal to the weight of the disappeared sulphur. From this it seems to follow that about half the latter goes off as sulphurous acid, and the other half remains behind in the acid mixture in some combination—perhaps as sulphuric acid.

The mixture obtained after the above reaction is colourless, thick, and effervesces when mixed with water most violently, with evolution of dense fumes of hyponitric acid. When the mixture with water is made without access of air, a colourless gas is given off in large quantity, which in contact with air or oxygen instantly forms red vapours, and is consequently nitric oxide†. When a layer of water is carefully poured upon the acid liquid, some gas is disengaged where the liquids are in contact, and a dark blue liquid formed there. From these statements it is evident that the mixture in question behaves like a solution of Rose's sulphate of nitric oxide in oil of vitriol.

If more sulphur is added to an acid mixture consisting of 9 parts oil of vitriol and 1 part of the hydrate of nitric acid than the mixture can dissolve, and it is gently heated when the first violent evolution of sulphurous acid is over, the liquid assumes a deep indigo-blue colour, which persists for some time after cooling; this colouring sometimes occurs without any artificial application of heat.

When flowers of sulphur are shaken with an acid mixture of 2 parts oil of vitriol to 1 part hydrate of nitric acid at the ordinary temperature, sulphurous acid is likewise instantly disengaged; but very soon, instead of the blue iodide of potassium paste being deco-

* As above observed, 1 drop of the hydrate of nitric acid in 2 oz. of oil of vitriol causes the formation of a very perceptible quantity of sulphurous acid, when a little powdered sulphur is mixed with this oil of vitriol. This behaviour affords therefore a ready means of detecting very minute quantities of nitric acid in the first hydrate of sulphuric acid.

† This acid mixture will probably afford the cheapest and readiest means of preparing large quantities of nitric oxide.

lorized, colourless paste is turned blue on being held over the liquid; when this occurs, slight vapours of hyponitric acid are at the same time perceptible. A large quantity of the flowers of sulphur, added at once to the acid mixture, produces even in the cold a violent frothing in the course of a few seconds, arising principally from the disengagement of sulphurous acid; but at the same time red vapours are apparent over the foaming liquid. It is scarcely necessary to observe that the residuary acid effervesces violently with water, giving off nitric oxide. Before proceeding to another subject, I should state that the reactions described in this paragraph do not occur when the nitrosulphuric acid is mixed with even comparatively little water.

II. Powdered selenium gradually dissolves, on agitation with nitrosulphuric acid, in the cold, without evolution of gas and with formation of selenious acid; on the addition of water, the acid mixture disengages nitric oxide.

III. Phosphorus in a finely-divided state dissolves gradually at 32° in nitrosulphuric acid containing one-tenth nitric acid, without any perceptible evolution of gas or the mixture becoming coloured. As soon as the acid has dissolved any quantity of phosphorus, water produces an abundant disengagement of nitric oxide, and the mixture contains sulphuric acid, phosphoric acid, and some phosphorous acid.

IV. The behaviour of iodine towards nitrosulphuric acid is especially interesting. When 28 parts oil of vitriol and 8 parts of the hydrate of nitric acid are mixed, and 3 parts iodine added to the mixture, the latter dissolves on agitation very quickly even in the cold, without any evolution of gas or heat, or the mixture becoming darker coloured. If the nitrosulphuric acid has been shaken violently with the iodine for about 10 or 12 minutes without interruption, it assumes a light sulphur-colour, owing to the incipient elimination of a solid powder. When the acid mixture, after the greater portion of the iodine is dissolved, is set aside in a closed flask, it gradually deposits the above-mentioned yellow substance, and becomes perfectly clear. If all access of air has been prevented, the acid mixture is nearly colourless; in a contrary case, more or less yellow or brownish-red. The yellow substance, after being freed as much as possible from adherent liquid, possesses the following properties:—

1. Exposed to the air on a watch-glass, it quickly becomes brown, and then gradually quite white, and finally deliquesces to a colourless liquid, which contains iodic and sulphuric acids.

2. When the yellow substance is mixed with water, it suddenly becomes brown from separation of iodine. The liquid obtained is brownish, becomes colourless when heated, with disengagement of iodine, and now behaves like iodic acid containing sulphuric acid.

3. When the yellow powder is heated sufficiently, vapours of iodine are disengaged with violent effervescence.

4. Æther, dropped upon the yellow substance, disengages dense fumes of iodine, and solid iodine is simultaneously eliminated in con-

siderable quantity. Even the vapour of æther acts violently upon the yellow substance in the cold, disengaging vapours of iodine.

5. If the yellow substance is first stirred with a little water to a thin paste, and æther then added, this dissolves the iodine eliminated by the water, acquiring a dark brownish-red colour. If the iodiferous æther be decanted from the brownish semifluid substance, and the latter treated repeatedly with fresh æther, it becomes colourless, and we obtain an acid liquid, upon which the æther swims; and a pasty mass, which adheres to the bottom of the vessel, dissolves readily in water, and has a very acid taste. Both the acid liquid, as well as the pasty mass, consist of iodic acid contaminated with sulphuric acid, together with a substance the nature of which I am still ignorant of. When the acid liquid, which has been decolorized by means of æther, is mixed with some oil of vitriol, after the æther has evaporated the liquid becomes brown, and a comparatively large quantity of iodine separates from it, with evolution of an extremely pungent substance, which violently irritates the eyes. When highly concentrated nitric acid is added instead of the oil of vitriol, vapours of hyponitric acid are disengaged and iodine eliminated. When the acid liquid is heated alone, it acquires a reddish-brown colour, with separation of iodine, and disengagement of a peculiar substance possessing a very pungent odour and extremely irritating to the eyes. It smells precisely like æther or alcohol on slow combustion.

6. The yellow powder does not dissolve perceptibly in cold oil of vitriol, but does so when warmed, when a slight evolution of gas occurs. The liquid obtained is nearly colourless, and exhibits the following reactions:—Exposed on a watch-glass to moist air, it is coloured brown; water precipitates some iodine from it, and the aqueous mixture behaves like sulphuric acid containing iodic acid; sulphurous acid has no action upon it; when mixed with flowers of sulphur, it disengages even in the cold a considerable quantity of sulphurous acid, with elimination of iodine and formation of iodide of sulphur; selenium and phosphorus eliminate iodine. A number of metals, even silver, separate iodine even in the cold, but iodides likewise appear to be formed. When bars of cadmium, zinc, iron or silver are immersed in the liquid, they are instantly covered with a red-brown coating of precipitated iodine. Spongy silver instantly colours the liquid blood-red. Vapour of æther, when brought into contact with a cold solution, colours it brown-red, with elimination of iodine. When the liquid is heated, paste held over it is coloured blue; paper which has been written upon with phosphorus, brown. At a temperature near the boiling-point of the liquid, faint vapours of iodine escape; and if the heating is continued sufficiently long, the solution loses the property of becoming brown with water, imparting to cadmium a brown-red colour, and in fact, no longer reacts as if it contained iodine.

Before making any observation on the nature of the yellow substance, I must say a few words respecting the behaviour of anhydrous iodic acid to oil of vitriol. As is well-known, iodic acid does not dissolve perceptibly in cold oil of vitriol, but it does in warm.

In dissolving, a faint disengagement of oxygen occurs, and a nearly colourless liquid is obtained, which does not deposit any iodic acid in the cold, and exhibits all the reactions which are peculiar to the solution of the yellow substance in oil of vitriol. That the iodic acid does not dissolve unaltered in oil of vitriol is proved from the circumstance that some iodine is eliminated from this solution by water. In all probability an oxide of iodine is formed under these circumstances, which contains less oxygen than iodic acid; and it is possible that a compound of this oxide and sulphuric acid is contained in a solution of iodic acid in oil of vitriol; but whatever be the nature of this compound, so much is certain, that it cannot exist in the presence of water, being decomposed into sulphuric acid, iodic acid and iodine. It would appear therefore that the yellow substance above described consists principally of free iodic acid mixed with that compound which is formed on dissolving iodic acid in hot oil of vitriol.

The liquid from which the yellow substance is deposited possesses the following properties:—It becomes brown when exposed to a moist atmosphere, with elimination of iodine. When mixed with water, it assumes a yellowish-brown colour, with elimination of iodine and violent disengagement of nitric oxide; when warmed, the aqueous mixture becomes colourless, and now behaves like sulphuric acid containing iodic acid. Anhydrous sulphurous acid has no action on the liquid. When mixed with flowers of sulphur, it disengages at the ordinary temperature sulphurous acid, with elimination of iodine and formation of iodide of sulphur. Phosphorus likewise separates iodine from the liquid; cadmium and zinc, &c. are covered with a brownish-red coating. Solution of potash separates iodine from the liquid, with disengagement of brownish-red vapours; æther and its vapour equally liberate iodine; for instance, when a strip of asbestos is saturated with the acid mixture, and held into a flask containing vapour of æther, iodine vapour is immediately disengaged with a hissing noise. When the liquid is heated in a dish, it becomes dark, and dense fumes of hyponitric acid escape; if the liquid has been kept boiling a few minutes, the disengagement of hyponitric acid ceases, and it becomes nearly colourless. When the application of heat is continued for some time, starch-paste held over the liquid is coloured blue. On allowing it to cool, after the evolution of brownish-red vapours has ceased, the liquid presents all the reactions peculiar to a solution of the yellow substance, or of iodic acid in oil of vitriol.

It is evident from the preceding statements, that the nitrosulphuric acid from which the yellow substance separated behaves in the first place as a solution of the so-called sulphate of nitric oxide in the hydrate of sulphuric acid, for with water it disengages nitric oxide; and secondly, as a solution of the yellow substance or iodic acid in oil of vitriol; for water separates iodine from it, and in the aqueous mixture we find sulphuric and iodic acid.

From all these facts it appears to result—

1. That a portion of the iodine mixed with the nitrosulphuric acid

is oxidized even in the cold to iodic acid; and another portion of the iodine is likewise oxidized, and enters into combination with sulphuric acid, which is partly deposited along with iodic acid in the form of the yellow substance above described, and partly remains dissolved in the sulphuric acid.

2. That in consequence of the oxidation of the iodine, sulphate of nitric oxide is formed, which equally dissolves in the oil of vitriol.

Before concluding this communication, I may be allowed to make a few observations upon the facts discussed. According to the views entertained on the nature of the hydrates of sulphuric and nitric acids, it must be admitted that the above-mentioned effects of oxidation of the nitrosulphuric acid arise from 1 atom of the hydrate of nitric acid parting with 3 atoms of oxygen, which combine with the sulphur, selenium, phosphorus or iodine, to form sulphurous, selenious, phosphoric or iodic acids; and it must be imagined that the separation of this oxygen is caused, on the one hand, by the affinity of the sulphuric acid for nitric oxide, and on the other, from the affinity of the sulphur, selenium, phosphorus and iodine for the oxygen. Now although I will not deny that such an assumption is capable of explaining the phænomena in question, there are some facts which do not appear to me to be quite favourable to it: I will only mention the formation of the sulphurous acid. We have seen that this acid is formed abundantly even at 32° on mixing flowers of sulphur with nitrosulphuric acid; now we should expect, under these circumstances, that instead of sulphurous only sulphuric acid would be formed. But since, as above stated, half the sulphur mixed with the nitrosulphuric acid is converted into sulphurous acid, it appears to me that it is not an immediate but a secondary product. It is possible that peroxide of hydrogen combines with sulphur, and that this compound is decomposed into water and sulphurous acid. This view is supported by the fact, that sulphur treated with an acid mixture, consisting of 2 parts oil of vitriol to 1 of nitric acid, sometimes disengages nitric oxide, which might be owing to the action of the water formed under these circumstances upon the sulphate of nitric oxide; however, I place no great value upon this opinion. If it be admitted that, on mixing the first hydrates of sulphuric and nitric acids, sulphate of nitric oxide is formed, an assumption which is not very hazardous, then it must be conceded, in accordance with the theory of the present day, that peroxide of hydrogen is formed, as no oxygen is given off on mixing the hydrates in the cold:—

$$2(SO^3 + HO) + NO^5 + HO = 2SO^3 + NO^2 + 3HO^2.$$

It has long been known that the hydrate of nitric acid, mixed with oil of vitriol, acts far more powerfully upon essential oils than alone. This fact proves that in this mixture the nitric acid is not merely in a mixed state; and it appears to me as if the fact were more satisfactorily explained by my hypothesis than by assuming that the presence of the oil of vitriol increases the oxidizing power of the nitric acid, from attracting the water of the nitric acid, and thus rendering it more inclined to part with another portion of its oxygen. As I have elsewhere endeavoured to show, the existence of NO^5 is ex-

tremely improbable, and consequently also the presence of water in that substance, which chemists call the first hydrate of nitric acid. But if there is no such thing as nitric acid, no hydrate of it can exist, and the ideas at present entertained respecting the mode of action of oil of vitriol upon highly concentrated nitric acid cannot be correct. I will just mention a fact here, which I intend some other time to discuss more fully, viz. that a mixture of the first hydrates of sulphuric and nitric acids disengages, when exposed to the light of the sun, neither hyponitric acid nor a perceptible quantity of oxygen, while according to my observations the first hydrate of nitric acid is evidently decomposed at a low temperature, and even in diffused light.

Whatever be the fate of the views expressed, they at least show that it is well to abstract sometimes from prevailing theories, and to endeavour to consider even the best-known things in a new point of view. This has the advantage of leading to experiments which would not be performed were we to place such implicit faith in the correctness of the chemical doctrines of the day; it certainly would not have occurred to me to have made the above experiments with nitrosulphuric acid, if I had not considered it possible that the hydrates of sulphuric and nitric acids might prove to be something different to what they are said to be; and in whatever way the ascertained facts may be interpreted, they are at least worth knowing, as they increase our knowledge respecting the behaviour of bodies to one another, the reactions of which appeared to be almost completely known.—Poggendorff's *Annalen*, Jan. 1847*.

On some Combinations of Nitric and Hyponitric Acids. *By* C. Gerhardt.

Some time since Prof. Graham advanced a theory of the basic salts, founded on the constitution of the basic nitrate of copper, which according to him is $3CuO, NO^5, HO$, while the neutral salt is $CuO, NO^5, 3HO$; and he considers the 3 equivs. of oxide of copper in the basic salt analogous to the 3 equivs. water of crystallization in the neutral salt, and capable of taking their place, but not of the basic water of the acid. Gerhardt, however, found quite a different amount of water in his experiments to that obtained by Graham. Graham's formula requires 65·5 per cent. oxide of copper and 4·9 water; Gerhardt found as the mean of eight analyses 66·2 per cent. oxide of copper and 11·9 water; the formula of this salt must consequently be modified; that corresponding to the results is $4CuONO^3\,3HO$; it requires 66·3 oxide of copper and 11·4 water.

Just as the neutral salt parts with only a certain portion of its water *in vacuo*, the basic salt likewise does not lose the whole of its water without being decomposed. Two different forms of the neutral salt are known, caused by a different amount of water; the one with the largest amount is pale blue, and possesses the formula

* This paper is dated Feb. 7, 1846; but, for certain reasons well known to the reader, its publication has been delayed by the author.

$CuO, NO^5 + 6HO$; the other, which Graham represents by $CuONO^5 + 3HO$, gave, on repeated analysis, an amount of water not corresponding to this formula, but to $CuO, NO^5 + 4HO$, which requires 30·7 per cent. oxide of copper, and Gerhardt found in two analyses 31·2; the facility with which this salt parts with some of the water explains the slight excess in the amount of oxide of copper found.

The nitrates of the magnesian series to which the copper salt belongs do not exist in the anhydrous state. The nitrates of the potash series (K, N, Pb, Ag, Ba), do not crystallize without water. The same relation therefore exists in this case as between monobasic and tribasic phosphates. This difference in constitution of the two series of salts is confirmed in other respects, for the nitrates of the potash series have a neutral reaction, and on decomposition by heat part first with oxygen, the salt being converted into a nitrite, while the salts of the magnesian series immediately part with nitric acid and are changed into basic salts; moreover their solutions have an acid reaction, like those of tribasic acids. The two series differ as markedly by these characters as the metaphosphates from the tribasic phosphates. The combinations of nitric acid with the peroxide and protoxide of mercury also belong to the tribasic type; they cannot be obtained anhydrous. If we adopt Gerhardt's mode of designating the protoxide of mercury by Hg^4O, and the peroxide by Hg^2O, we may imagine H to be replaced by Hg in the salts of the oxide, and H by Hg^2 in the protosalts. For example, if we designate by Hgα Gerhardt's Hg, and by Hgβ his Hg^2, we have—

The dimorphous protonitrate.....	$= N(HHg^2\beta)O^4$.
The crystallized oxide	$= N(HHg^2\alpha)O^4$.
Brook's salt of mercury	$= N(Hg\beta Hg\alpha^2)O^4$.

According to Gerhardt's experiments, only two basic nitrates of lead exist. When the solution of the neutral salt is boiled with litharge or treated with ammonia, the one salt separates in the form of slender thin needles; this salt is $2PbONO^5 + HO$, which requires 78·0 oxide of lead and 3·2 water; the author found 77·8 oxide of lead and 3·3 water. This basic salt loses between 392° and 518°, only pure water, which it most firmly retains at 212°; consequently it may also be arranged in the tribasic series, when it will correspond to the neutral phosphate of soda, $(2PbO, HO) + NO^5$, resembling $(2NaO, HO) + PhO^5$. It is converted by drying into a salt analogous to the pyrophosphate of soda, from which it differs only in being less stable.

The second basic nitrate of lead is obtained by precipitating the neutral salt with an excess of ammonia; the precipitate is collected on a filter, and well-washed to remove the preceding salt; when this is done, a yellowish residue is left, which appears under the microscope to consist of rectangular tablets with truncated edges. This residue is washed once more with some boiling water, to which a minute quantity of nitric acid has been added in order to remove

any carbonate of lead that may have fallen, and then dried at 212°. The analysis of this precipitate yielded on an average—

Oxide of lead	84·7	84·7
Water	5·1	5·6

leading to the formula $4PbO, NO^5 + 3HO$. This salt parts with its acid on boiling with ammonia, the oxide being converted into hydrated oxide; but on long-continued boiling this becomes reddish.

When nitrate of lead is boiled with metallic lead, the first salt obtained is one which crystallizes in orange-yellow scales, which Peligot regards as a basic hyponitrate of lead. On preparing this salt by passing hyponitric acid into water in which finely-divided litharge was suspended, it was obtained of the same composition as that prepared according to the first method. Two analyses of the salt, obtained according to the first method, yielded 80·3 and 80·4 per cent. oxide of lead; one analysis of the salt, prepared according to the last method, gave 80·0 per cent. oxide; Peligot's formula, $2PbO, NO^4, HO$, requires 80·3. Although the salt, which might likewise be regarded as a combination of nitrite of lead with nitrate, can be obtained directly by the contact of the vapour of the hyposulphuric acid with oxide of lead diffused in water, its type is nevertheless very inconstant, and it is impossible to prepare from it the other hyponitrates by mutual decomposition.—*Ann. de Chim. et de Phys.*, xviii. p. 178.

On the Occurrence of Saponine. By M. Malapert.

The author, conjointly with M. Bonnet, has shown that *Saponaria officinalis* and *Agrostemma Githago* are poisonous, and ascribes this to their containing saponine. In the last plant the saponine occurs principally in the ripe and immature seed, and also in the roots, but the other parts contain none. *Silene nutans* contains at least as much saponine as *Saponaria*, but here it is diffused throughout the plant except in the seed; the author, moreover, found this principle in *Dianthus caryophyllus, D. Cæsius, D. carthusianorum, D. proliferus* (chiefly in the roots, less in the leaves, and not at all in the flowers and seed), *Lychnis dioica, L. chalcedonica, L. flos cuculi, Silene inflata, Cucubalus Behen*, and in *Anagallis arvensis* and *A. cærulea*, but not in *Arenaria, Stellaria* and *Holosteum*. Fremy found saponine in the horse-chestnut; the author has also detected it in the fruit, but in no other part of the tree.—*Journ. de Pharm.*, x. p. 339.

On the Action of Sulphuretted Hydrogen upon Nitrous and Nitric Æthers. By E. Kopp.

In a memoir in which the author discusses the artificial formation of organic alkalies, he has published several experiments relative to the reduction, by sulphuretted hydrogen, of nitrous and nitric æther.

The nitrous æther was prepared by allowing equal volumes of alco-

hol and nitric acid to act upon each other in the presence of iron or copper filings. The action is never violent, even when large quantities are operated upon, and is effected almost without any application of heat. The vapour of the nitrous æther is washed by passing it through a flask filled with water, then through a long tube filled with chloride of calcium to dry it, and is condensed in a small balloon kept cool by a good refrigerating mixture. The product thus obtained is perfectly pure and free from aldehyde, which is easily ascertained by treating it with potash, which does not occasion any brown colouring. In this process the copper evidently reduces the pure nitric acid to the state of hyponitric acid, which in the nascent state acts upon the alcohol.

Nitrous æther is very easily reduced by sulphuret of ammonium; immediately the two bodies are brought together an extremely violent reaction ensues, which is completed in one or two minutes; sulphur is eliminated, and when the product is distilled after having separated the precipitate, a strongly ammoniacal liquid passes over. When neutralized with hydrochloric acid and again submitted to partial distillation, it yields an alcoholic liquid with a very faint oniony smell. The residue consisted solely of chloride of ammonium, the action is therefore as follows :—

$$C^4\,H^5\,NO^4 + 6HS = C^4\,H^6\,O^2 + 2HO + NH^3 + 6S.$$

Nitric æther is reduced far more slowly than the preceding, and as it is less volatile the reaction is more easily observed. When sulphuretted hydrogen is passed into nitric æther diluted with an alcoholic solution of ammonia, the mixture gradually becomes heated up to 95°–105°. The colour of the liquid then darkens, and very soon minute needles of sulphur make their appearance, the quantity of which rapidly increases, so that if the æther had not been diluted with alcohol the whole would form a thick paste. On distilling the alcoholic liquid, the residue is found to contain only traces of nitrate of ammonia, but the distillate contains ammonia and mercaptan.

Nitric æther likewise furnishes this latter product when reduced by the sulphuret of ammonia, without the intervention of alcohol. The reaction, therefore, is

$$C^4\,H^5\,NO^6 + 10HS = C^4\,H^6\,S^2 + NH^3 + 6HO + 8S.$$

Revue Scientifique, xxvii. p. 273.

On a safe and easy Method of preparing Chlorous Acid. *By* Dr. J. E. de Vry.

In attempting to prepare chloric acid by mixing solutions of equal equivalents of tartaric acid and chlorate of potash, I obtained, on the cooling of the hot solution, instead of the expected bitartrate of potash, a double salt consisting of chlorate and tartrate of potash. The mother-ley, which was very acid, contained free chloric and tartaric acids, and yielded, on boiling in a retort, a considerable quantity of chlorous acid, which was contaminated only by carbonic acid.—Liebig's *Annalen*, Feb. 1847.

On the Action of Nitric Acid upon Oil of Turpentine.
By A. Cailliot.

To answer the question, whether resins are formed in plants or are products of decomposition of the essential oils, the author subjected oil of turpentine to various methods of oxidation, as by exposure to the air, exposure to the air in the presence of bases, and oxidation by nitric acid; the products obtained by the latter method of oxidation are very numerous. Nitrous vapours are given off, together with carbonic acid, a tolerable quantity of prussic acid, and a certain amount of almost unaltered oil of turpentine. The mother-ley remaining in the retort has been examined by Bromeis and Rabourdin*; the former discovered a peculiar acid in it, turpentinic acid, the latter in addition oxalic acid, and in several cases quadroxalate of ammonia. The author found it to contain oxalic acid, prussic acid, which appears to occupy the place of oxalate of ammonia, turpentinic acid and three new acids. The first of these has the formula $C^{16}H^6O^3 = C^{16}H^4O^6 + 2HO$, and is consequently isomeric with the phthallic acid discovered by Laurent; the author has named it *terephthalic acid*; it is sufficiently distinct from phthallic; it is white, tasteless, insoluble in water, alcohol and æther; when heated, a portion sublimes without parting with its hydrate water, while another portion is decomposed into carbonic acid and benzole, $C^{12}H^6$. The acid is entirely converted into benzole and carbonic acid when heated with hydrate of lime. Nearly all the salts of terephthalic acid crystallize and burn readily, diffusing the odour of benzole.

The second acid, $C^{14}H^7O^4 = C^{14}H^6O^3 + HO$, *terebenzic acid*, only differs from benzoic acid by one additional equivalent of hydrogen, and in other respects resembles it very closely. Like that acid, it is volatilized previously to melting, dissolves sparingly in cold, more readily in boiling water, and separates on cooling in acicular crystals. The salts of the new acid exhibit the same solubility as the corresponding benzoates. Notwithstanding these analogies, it is impossible to confound the two; and the terebenzic acid is decomposed in boiling water, and forms on crystallization a confused mass of needles, and not laminæ like benzoic acid; moreover, the terebenzic acid melts at 336°, benzoic acid at 248°; terebenzic æther possesses a very distinct odour of aniseed, and its boiling-point is situated at 266°, 38° higher therefore than that of the benzoic æther.

The third acid contained in the mother-ley, *terechrysenic acid* ($C^6H^4O^5 = C^6H^3O^4 + HO$), differs essentially from the two preceding; it forms an orange-yellow amorphous mass, is very deliquescent, and dissolves in every proportion in water, alcohol and æther; its taste is at first strongly acid, and subsequently astringent and bitter. It expels acetic acid from its combinations, and forms with a large number of bases salts soluble in water. The acid is not volatile; it is decomposed on distillation, first into carbonic acid and

* See Chem. Gaz., vol. iii. p. 285.

a slightly coloured liquid acid, subsequently into combustible gases and an oily yellowish substance, and leaves a compact coal. The æther of this acid is a dark orange-coloured viscous liquid, which yields on distillation an æthereal, nearly colourless liquid, an oily liquid and a residue of carbon.

The resinous mass which separates from the mother-ley still contains considerable quantities of terephthallic and terebenzic acids, and three substances which in their physical and chemical properties are allied to the natural resins. The first, $A = C^{40} H^{24} O^{20}$, is insoluble in alcohol and alkalies, and corresponds to the subresins; the second, $B = C^{40} H^{20} O^{10}$, is soluble in alcohol, insoluble in alkalies, and corresponds to the neutral resins, for instance abietine; the third, $C = C^{40} H^{24} O^{16}$, dissolves in alcohol and in alkalies, and exhibits great resemblance to colophony. Although the properties of these resins resemble those of the natural resins, yet their composition distinguishes them from the latter, as they contain more oxygen and less hydrogen. Some experiments led the author to the view that the natural resins likewise afford analogous products when acted upon with nitric acid. In the reaction of nitric acid upon pimaric acid, a substance was obtained which was insoluble in ammonia, soluble in alcohol, and appeared to be identical with the body B. According to the formulæ of the above-mentioned substances, they may be arranged in two series, the first of which comprises those containing less than 20 equivs. carbon, while the second includes those resinous bodies which contain 40 and more equivs. carbon.—*Comptes Rendus*, xxiii. p. 920.

On the Existence of a new Oxyacid of Nitrogen, and on the Theory of the Manufacture of Sulphuric Acid. By C. H. Barreswil.

The author endeavours to prove that the blue liquid which is obtained on condensing by cold a moist mixture of hyponitric acid and binoxide of nitrogen, is neither nitrous acid nor a mixture of binoxide of nitrogen and hyponitric acid, but a definite compound, the probable formula of which is NO^7, corresponding to permanganic and perchromic acids.

One of the most convincing proofs that the blue oxyacid of nitrogen is not nitrous acid is its behaviour towards concentrated sulphuric acid, which instead of simply combining with it, as would happen were it nitrous acid, instantly decomposes it, producing the crystalline combination of sulphuric acid and nitrous acid, and at the same time a considerable disengagement of hyponitric acid.

This compound, to which from analogy of composition the author has given the name of *pernitric acid*, has hitherto not been obtained in combination with bases; it has however been ascertained that it contains constitutional water, although it is decomposable by water.

The author then enters into some considerations concerning the manufacture of sulphuric acid. Three theories are current among chemists, that of Messrs. Clement and Desormes, that of Berzelius, and that of M. Peligot. The theory proposed by M. Barreswil

differs from, or rather combines all three. Starting from certain facts, which the author discusses, the following propositions may be established:—1st, the binoxide of nitrogen and sulphurous acid combine in the presence of air to form the compound $SO^3\,NO^3$; 2nd, this compound being very unstable, is decomposed by the water, according to the quantity of the latter present, either into hyponitric acid and deutoxide of nitrogen, or into nitric acid and deutoxide of nitrogen, or lastly into pernitrous acid and deutoxide of nitrogen; 3rd, the hyponitric acid regenerates with the sulphurous acid the combination $SO^3\,NO^3$, and consequently binoxide of nitrogen; 4th, the nitric acid forms with the deutoxide of nitrogen pernitrous acid; which finally produces with the sulphurous acid deutoxide of nitrogen and sulphuric acid.

Thus the absorption of oxygen by the sulphurous acid depends not on direct oxidation, but, on the one hand, on the successive formation and decomposition of a compound $SO^3\,NO^3$; and, on the other hand, on the reaction of the binoxide of nitrogen on the atmosphere, and of this gas, and of the nitrous acid upon the nitric acid.

M. Barreswil admits, with the partisans of the first theory, the existence of an unstable compound; but it is not necessary, in his opinion, that this compound should exist in the crystalline state; it may just as well be in solution in the sulphuric acid which is introduced in the course of the manufacture, or exist ephemerally in suspension in the atmosphere of the chambers. He admits, with Berzelius, the necessity of the formation of a highly oxidizing body; but he believes this compound to be the hyponitric and not nitrous acid. And lastly, he admits, with M. Peligot, that the formation of the nitric acid is a necessary result, but denies that this acid is directly attacked by the sulphurous acid, and believes that it is only reduced because previously decomposed by the deutoxide of nitrogen, with which it forms either hyponitric or pernitrous acid, which are the sole oxidating agents.—*Comptes Rendus*, Sept. 21, 1846.

ANALYTICAL CHEMISTRY.

On a new Process for estimating Phosphorus. By M. Raewsky.

The quantitative determination of phosphorus is one of the most delicate and tedious operations of analytical chemistry; and it is principally on this account that comparatively few analytical investigations have been made on the compounds of phosphorus. I have therefore considered that it would be of interest to science and useful to analysis to discover a quick and accurate method for estimating this substance. The new process consists in bringing the phosphorus to the state of pure perphosphate of iron, which is collected, and the amount of iron in it determined. I have ascertained the composition of this salt by a numerous series of experiments; and the

quantity of iron being known, I calculate the proportion of phosphoric acid. The tedious and delicate operations of drying, calcining and weighing are avoided, and one hour is more than sufficient for a complete analysis. I estimate the iron in the perphosphate by the method of M. Marguerite. Any other oxidizing body might be substituted for the mineral chameleon; but this is of no importance, and no other compound is so sensitive. I shall not describe the course to be followed in order to isolate the phosphoric acid from the substances which accompany it; the processes must vary according to the nature of the substances, and are subject to the ordinary conditions of analytical chemistry. I believe it will always be easy to obtain this object, except perhaps when the substance to be analysed contains alumina; but in this particular case we can always have recourse to the ingenious process described by M. Fresenius. I proceed as follows:—After having separated the phosphorus from the bases with which it might combine and yield salts insoluble in acetic acid, I add to the liquid, which is generally acid, an excess of a solution of peracetate of iron*. The phosphate of iron immediately separates in the form of slightly yellowish light flakes, the precipitate is collected and carefully washed. The excess of iron passes off in the washing, and the pure phosphate is left on the filter. This done, I drop hydrochloric acid on to the filter, so as to dissolve the whole; reduce the salt of iron by means of sulphite of soda, following the precautions indicated by M. Marguerite; I then determine the amount of iron by converting it into peroxide with a solution of known strength of mineral chameleon. Having determined the quantity of iron by a simple calculation, knowing the composition of the perphosphate of iron, I easily find the proportion of the phosphorus.

In the perphosphate of iron which is formed in a solution containing an excess of acetic acid, the relation of the oxygen of the base to the oxygen of the acid is as 3 to 5, as I have convinced myself by numerous experiments made with the pure salt. In all the assays made in the presence of variable quantities of acid and under different circumstances upon different weights of substance, I always obtained perfectly identical numbers. I insist upon this point, because the process is wholly based upon the accuracy of the analysis of the perphosphate of iron.

I have stated that the proportion of iron being known, the phosphorus might easily be determined by a simple calculation; this will be best seen by an example. I will select the analysis of the phosphate of soda. Suppose that, having operated upon 0·466 grm. of this salt, 15 divisions of the normal solution have been employed,

* Instead of employing the peracetate of iron, which is not permanent, I form a solution of 100 grms. of iron-alum in water, so that the volume of the liquid occupies 1 litre; and I make a similar solution of acetate of soda (according to theory 98 grms. form an equivalent proportion). In this way I form the acetate by double decomposition at the very moment it is called into action.

the strength of which is 54·4 divisions for 0·250 of iron, I then find the iron by the proportion

$$54{\cdot}4 : 0{\cdot}250 :: 15 : X = 0{\cdot}069 \text{ of iron.}$$

On the other hand, the composition of the phosphate of iron being known, I say

$$700\ Fe^2 : 900\ PO^5 :: 0{\cdot}069\ Fe : X ;$$

and I find that 0·069 of iron correspond to 0·0887 phosphoric acid. Now in 1 grm. of phosphate of soda there is 0·191 phosphoric acid; consequently, to convert this into phosphate of soda, I make the following calculation:—

0·191 : 1 grm. phosphate of soda :: 0·0887 acid : X = 0·464 grm., instead of 0·466 grm., which was submitted to analysis.

To appreciate the degree of precision of this process, I have submitted it to numerous severe tests, and the results found were always accurate to within 6–8 thousandths.—*Comptes Rendus, April* 19, 1847.

On Pelouze's *Test for Lactic Acid.* *By* Dr. A. Strecker.

In vol. iii. p. 29 of this Journal we gave the reaction proposed by Pelouze as a test for lactic acid, viz. the imperfect precipitation of a solution of lactate of copper; hence its non-decolorization by the addition of milk of lime. As this reaction has been used in several instances to determine the presence of lactic acid in fluids, as by Bernard and Barreswil in the gastric juice, by Boussingault in the urine of the Herbivora*, and by Gobley† in the yolk of egg, it was a matter of interest to test its correctness and applicability.

For this purpose, the author treated an aqueous solution of pure lactate of copper with milk of lime free from potash, and found that, on the addition of but little milk of lime, still so much that lime remained suspended in the fluid, the filtered solution assumed a pale blue colour, whilst on the application of a little more milk of lime it became perfectly colourless. When treated with a few drops of muriatic acid and some sulphuretted hydrogen, the solution yielded a troubling so slight that it could only be perceived by looking perpendicularly through the test-tube. When the colourless solution which contained the small quantity of oxide of copper in solution was again treated with a little milk of lime and filtered, it did not give the slightest reaction on the addition of sulphuretted hydrogen or ferrocyanide of potassium. If freshly-precipitated hydrated oxide of copper be added to a solution of lactate of lime, it is dissolved, but completely re-precipitated by milk of lime. Hence the presence of lactic acid renders the complete precipitation of the oxide of copper difficult, but does not prevent it; moreover there are a large number of organic bodies *which do the same*; Pelouze mentions saccharine substances only. The author found this to occur with gela-

* Ann. de Chim. et de Phys., 3rd ser. t. xv. p. 97.
† Chem. Gaz. vol. iii. pp. 443, 486.

tine, glycocolle, impure lactate of lime, muriate of ammonia, cane- and grape-sugar, gelatine after ebullition with potash, fibrine, albumen and caseine; with the last six of these bodies the solution was intensely coloured.

Hence, although the author does not deny the existence of lactic acid in urine, the yolk of egg, &c., he considers it not proved by the experiments of Boussingault and Gobley; moreover, he thinks that on a more extensive application of this test, lactic acid will be admitted to exist in a number of fluids in which it is entirely absent. —Liebig's *Annalen*, Bd. lxi. Heft 2.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Theory of Dyeing, and its application to various processes in general use, and more particularly that kind of Dyeing with Indigo, called Vat-dyeing. By M. Chevreul.

In this paper (which forms one of a series presented by M. Chevreul to the Académie des Sciences) the author states the following facts, and draws the conclusions which will be found at the end of this article. The colouring matters by which fabrics made of organic matters are dyed, are fixed therein in three states,—1st, in a state of chemical combination; 2nd, in a state of simple (or mechanical) mixture; 3rd, a portion of the colouring matter is in a state of combination, whilst the remainder is in a state of simple mixture.

M. Chevreul then treats of the process of dyeing, as regards chemical combination, relatively to two circumstances attending the practical operation of the same.

A. Respecting the temperature,—1st, that of the atmosphere; 2nd, boiling heat; 3rd, an intermediate temperature.

There are, therefore, three methods of dyeing—the *cold process*, the *boiling process*, and the *warm process*.

B. Respecting the number of substances immersed, it is minimum when there is only the water, the colouring matter and the fabric; the number is maximum when there is—1st, water, which may hold in solution either an alkaline or acid substance, or a neutral body; 2nd, one or more colouring matters; 3rd, the fabric to be dyed; 4th, a substance called a mordant, the nature of which may be more or less complex.

M. Chevreul gives numerous examples of dyeing processes, considered as regards the above points; and examines the theory of Macquer regarding colouring matters, and the mode of fixing them, either with or without mordants. After demonstrating the incorrectness of this theory, he defines the art and science of dyeing from personal experiments, and insists upon their intimate connexion with chemistry.

He applies himself most particularly to demonstrate the influence of heat in fixing colouring matters in fabrics, when operating either in a boiling bath, or by means of steam. He shows the identity of the results in the two methods of fixing the colours, with this difference,—that a much larger quantity of water and mordant must be used with the boiling process, than when employing steam to fix a colouring matter, which had been thickened before printing.

M. Chevreul observes, that in certain cases, the substance used for thickening the colouring matter and the mordant acts as a preservative to the fabric, by weakening the corrosive action of the mordant. He is also of opinion, that in many cases where the boiling process is employed, steam may be much more advantageously used.

M. Chevreul also demonstrates, that by fixing indigo by the warm process upon wool, and by the cold process upon cotton, much advantage will be derived from the action of steam, and also by boiling in alum and tartar, as the fixity of the colour is thereby remarkably increased. He considers the process of dyeing with indigo, as at present practised, principally on woollens, by the warm method and without mordant, to be very imperfect.

The author thinks himself justified in drawing the following conclusions from the result of the experiments described in his memoir, viz.—

Felted cloth dyed in a blue-stone vat, is much improved by being treated with steam, or passed through a boiling solution of alum and tartar, or by passing it through water containing a mixture of scarlet and alum, also boiling; the first two processes are, however, preferable to the third.

Mousseline-de-laine, treated with bran, or passed through sub-carbonate of soda or lime, furnished precisely similar results. It was also shown that the action adds to the effect of the aluming process.

Analogous results were obtained with cotton, but the steam and aluming processes do not fix the colour upon ligneous fibres so well as upon woollens. This was shown on inspecting the samples of cotton and wool dyed with indigo, submitted to the Academy, and which were exposed to the atmosphere during the same space of time.

The questions which arise from the foregoing, are,—1st, whether in all cases where the cold process has been employed, either with or without a mordant, the colour would not be better fixed by boiling? 2nd, whether, in all cases where the hot process has been employed without a mordant, a much better effect would not be produced by adding a mordant?

M. Chevreul concludes his memoir by an observation which leads us to hope that colours may be much better fixed than at present, both in dyeing and printing, by the addition of certain substances which are not mordants, as he has already shown that gum-arabic and several other analogous substances, and also some fatty bodies,

will fix indigo-blue upon the fabrics independently of the boiling process or of a mordant.—*Comptes Rendus, &c.*, as inserted in the *London Journal of Arts.*

PROCEEDINGS OF SOCIETIES.

Royal Institution.

April 20. (W. R. Hamilton, Esq., V.P., Treasurer, in the Chair).

"On the preparation of India-rubber by Vulcanization and Conversion," by Mr. Brockedon.

Mr. Brockedon's object in this communication was to describe,—1st, a mode of treating india-rubber by which new properties are imparted to this substance; 2nd, the new uses in the arts to which these acquired properties now render india-rubber applicable. *Vulcanization* and *conversion* denote that combination of india-rubber with sulphur from which the new properties about to be described result. The process of conversion consists in submitting india-rubber to the action of bisulphuret of carbon mixed with chloride of sulphur. The caoutchouc cannot, however, be penetrated by this process to any depth; and therefore it is inapplicable when the mass to be acted on is thick. The process of *vulcanization*, which seems to be more applicable, is the result of many experiments made by Mr. Hancock; who found that caoutchouc, when immersed in a bath of fused sulphur heated to various temperatures, by absorbing the sulphur, assumed a carbonized appearance, and lastly acquired the consistency of horn. It was in the course of these changes that it attained the state of vulcanization which Mr. Brockedon afterwards described. The same vulcanized condition can, however, be produced either by kneading the india-rubber with sulphur and then exposing it to a temperature of 190°, or by dissolving the india-rubber in any known solvent, as turpentine, previously charged with sulphur. Having thus explained the processes, Mr. Brockedon described the effect which they produced on the caoutchouc:—1st, the india-rubber, thus treated, remains elastic at all temperatures; in its ordinary state it is quite rigid at a temperature of 40°; 2nd, vulcanized caoutchouc is not affected by any known solvents, as bisulphuret of carbon, naphtha, or turpentine; 3rd, it is not affected by heat short of the vulcanizing point; 4th, it acquires extraordinary powers of resisting compression. Thus, a cannon-ball was broken to pieces by being driven through a mass of vulcanized caoutchouc—the caoutchouc itself exhibiting no other trace of its passage than a scarcely perceptible rent. The applications of this substance appear to be almost infinite. Our readers are familiar with the usefulness of the "elastic bands;" but they may not be aware that the same fabric, adjusted in size and strength to the purpose required, furnishes springs for locks and for the racks of window-blinds. It is also capable of being moulded into the most intricate ornaments; its characteristic elasticity removing

all embarrassment in relieving the undercut parts. It furnishes impervious bottles for volatile substances, like æther; as well as an excellent ink-stand. It is adapted to protect from corrosion, wires subjected to the action of the sea, as in the case of the wires required for the projected electric communication between England and France. For the same reason, air-tubes of vulcanized rubber are better suited for life-boats than those formerly made of canvas, which are liable to be destroyed by the action of the water. A similar tube has been used with success as a substitute for an iron band as the tire of a carriage-wheel; and it is stated that a vehicle so arranged runs much easier than on the present plan. But perhaps the most important application is in its use in railroads and railroad carriages. In the former, it is laid between the rail and the sleeper, and thus prevents the rails from indicating any traces of pressure; and the springs connected with the buffers of the latter, when formed of vulcanized caoutchouc, can neither be broken, nor can their elasticity be surmounted by any degree of concussive violence. In conclusion, Mr. Brockedon exhibited objects illustrative of the great physical change induced on caoutchouc by vulcanization. He showed a screw, with its recipient, both made of this substance, as well as a form of letter-press (like a stereotyped page) for printing. He also noticed its usefulness in making epithems for surgical purposes, gloves and boots for gouty persons, &c.

PATENT.

Patent granted to John Taylor, Adelphi, Middlesex, *for Improvements in the Manufacture of Explosive Compounds.*

This invention, which has already attracted so much notice under the name of "Schönbein's gun-cotton," consists in the manufacturing of explosive compounds, applicable to mining purposes, the throwing of projectiles, and otherwise, as substitutes for gunpowder, by subjecting matters of vegetable origin to the action of acids.

The substance which the patentee prefers to operate upon is cotton in the state in which it is brought to this country, but freed from extraneous matters, and perfectly dry. The acids used are nitric acid of from 1·45 to 1·50 spec. grav., and sulphuric acid of 1·85 spec. grav.; and these are mixed, in the proportion of 1 measure of nitric acid to 3 of sulphuric acid, in a vessel of glazed earthenware or other material not acted on by acids. By this admixture great heat is produced, and the mixture must be allowed to cool down to a temperature of 50° or 60° F. The cotton, in a loose, open state, is then put into the mixture; and, in order to ensure the thorough impregnation of the cotton with the acids, it is stirred with a rod of glass or other substance capable of resisting the action of acids; after which the mixture is drawn off. The cotton is gently pressed in the vessel containing it by a presser of glazed earthen-

ware or other suitable material, in order to expel part of the mixture, and is then covered and left for an hour; at the expiration of this time it is again pressed, to remove as much of the acids as is practicable; after which the cotton is washed in a continuous flow of water, by stirring it therein, until the water which runs off is found to be perfectly free from acid on testing it with litmus-paper. The cotton is now pressed to expel the water; and, in order to ensure the cotton being perfectly free from uncombined acid, it is dipped into a very weak solution of carbonate of potash (composed of 1 oz. of carbonate of potash to 1 gallon of water), and then subjected to pressure, to discharge the same. At this stage of the process, if the cotton were to be thoroughly dried, it would be highly explosive; but, to increase its strength, it is next immersed and thoroughly stirred in a weak solution of nitrate of potash, prepared by dissolving 1 oz. of nitrate of potash in 1 gallon of water; the use of the solutions of carbonate and nitrate of potash may however be dispensed with. The cotton is pressed to free it from the solution of nitrate of potash, and is then opened out and dried; the drying may be effected by spreading it thinly on surfaces in a room heated by steam or otherwise, to about 150° F. When dry, the cotton is ready for use.

Nitric acid alone produces on cotton a similar effect to that produced by the mixture of nitric and sulphuric acids; but when nitric acid is used, the cotton should be washed immediately after it has been soaked in the acid.

The patentee does not confine himself to the use of cotton; for other matters of vegetable origin may be converted into explosive compounds by the same acids; neither does he confine himself to the use of nitric acid or sulphuric acid of the specific gravity above mentioned.

With regard to the use of the explosive compound, 3 parts of it by weight will be equal in strength to, if not more powerful than, 8 parts by weight of Tower-proof gunpowder; and still less of the compound may be employed when it is substituted for gunpowder of an inferior quality. The explosive compound may be rammed into a piece of ordnance or a musket; or it may be made into cartridges; or, when slightly damp, it may be pressed in moulds corresponding to the different calibres of pieces of ordnance, fowling-pieces, &c., and after being dried it will retain the desired shape. When placed in caps, similar to the ordinary percussion-caps, the compound may be discharged by impact.—Sealed Oct. 8, 1846.

THE CHEMICAL GAZETTE.

No. CXIII.—July 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of Coffee Berries. By D. F. Rochleder.

In his former investigation on this subject*, the author obtained a substance which is extracted by water from the raw berries, and is precipitated by neutral acetate of lead with a yellow, by the basic acetate with a gray colour, which soon becomes green. In order to extract the berries well, they should be previously dried at about 140°, which renders them so brittle that they may be pulverized without difficulty. Æther extracts from the pulverized berries fat and caffeine, together with a small quantity of caffeic acid. The berries, exhausted with æther, yield a large quantity of legumine and some sugar† to water, and also a considerable quantity of caffeates. But the caffeic acid cannot be obtained perfectly pure in this manner; the dried and pulverized berries were therefore exhausted with boiling alcohol of 0·951 spec. grav., and the solution strained. On mixing it with twice its volume of water, a quantity of white flakes is precipitated, which, after drying and melting, constitute a brownish butter-like fat. The liquid, freed in this manner from the greater portion of fat, was heated to boiling, and a solution of acetate of lead added to it; the liquid was then boiled for a few minutes, when the precipitate became more aggregated. When the precipitation is made at the ordinary temperature, the precipitate is gelatinous, and cannot be filtered and washed except with the greatest difficulty. The precipitate is washed with dilute spirit, suspended in water, and decomposed by sulphuretted hydrogen; the faintly yellowish liquid is separated by filtration from the sulphuret of lead, and evaporated to dryness in the water-bath. In this manner a gummy mass is obtained, which retains very tenaciously the last portions of water; it required three days' drying at 212° to free it entirely from water. This acid has a faintly acid and at the same time somewhat astringent taste, dissolves readily in water, and is not precipitated by alcohol even from a syrupy solution. In the dry state, it is brittle and easily reduced to powder. It is soluble in sulphuric acid; when warmed, the colour becomes blood-red; on the

* Chem. Gaz., vol. ii. p. 505. † And a trace of albumen.

addition of water, small flakes are precipitated, and at the same time the liquid is decolorized. It dissolves in concentrated solution of potash with a reddish-yellow colour, which on the application of heat becomes pale yellow; it likewise dissolves in ammonia; the yellow colour turns green with absorption of oxygen, which may probably be owing to the presence of a trace of lime in the acid. The combinations of the acid with lime and baryta are yellow, but quickly become green by exposure to the air when the acid is not in excess. The acid is decomposed when heated upon platinum foil, leaving a large cinder, and giving off a peculiar disagreeable odour simultaneously with that of acetic acid. It burns with a bright flame. When the acid is heated in a glass tube, it likewise leaves a considerable residue of carbon, and at the same time diffuses a strong odour of burnt coffee. Dilute solutions are not precipitated by protosalts of iron or salts of lead; nitrate of silver produces in a moderately concentrated solution a precipitate, which soon becomes black; when warmed, the silver is deposited as a metallic mirror on the sides of the vessel. The acid, prepared in the manner above described and dried at 212°, presented the following composition:—

Carbon	56·58	56·47	16 =	1200·0	56·81
Hydrogen	5·50	5·58	9	112·5	5·32
Oxygen	37·92	37·95	8	800·9	37·87

It is difficult to obtain salts which are not altered in the air. The lime, baryta, potash, soda and ammonia salts absorb oxygen and assume a darker colour; the salts of lime and baryta become green during edulcoration if there is not an excess of free acid present; but in this case the salts are soluble, and when they are evaporated compounds are obtained containing an indefinite quantity of free acid; by the addition of alcohol, salts are obtained, which likewise change in the air, while a portion remains in solution with the excess of acid. To prepare a barytic salt of definite decomposition, a moderately concentrated solution of the acid was divided into two portions, the one saturated with barytic water, and then mixed with the other portion. This liquid was evaporated in the water-bath, and towards the end some alcohol added in small portions. When the liquid was so far evaporated that a drop became milk-white upon a cold plate of glass, and resinous flakes separated, it was strained through linen into a warm glass, by which means some of the flakes were removed, and then allowed to cool. The liquid solidifies to a colourless transparent jelly, which forms, after being pressed between linen and blotting-paper, dried at 212°, and reduced to powder, a grayish-yellow earthy mass, which yielded on analysis—

Carbon.....	46·29	32 =	2400·0	46·32
Hydrogen	4·57	18	225·0	4·34
Oxygen	30·69	16	1600·0	30·88
Baryta.....	18·45	1	956·9	18·46

When an excess of barytic water is added to an aqueous solution of the acid, a precipitate is formed, which with a small excess ap-

pears pale yellow, with a large excess dark orange-yellow, but on the filter becomes green and brown. It was found impossible to obtain a salt of copper of constant composition. The salts which are formed in acid solutions are gray, melt as long as they are dry at 212°, forming green resinous masses, and dissolve in water on the addition of some ammonia with a green colour, which becomes blue on the addition of more ammonia. The basic salts are more of a green colour. A solution of protosulphate of iron does not throw down any precipitate in the acid; but if some ammonia is added, an almost black precipitate results, which dissolves in acetic acid with a bottle-green colour. The copper and persalt of iron from different preparations always yielded on combustion the same relation of carbon to hydrogen as the free acid, but the amount of metallic oxide varied constantly.

When the pulverized coffee berries are exhausted with boiling alcohol, and the decoction mixed with water and filtered to separate the fat, the solution heated to boiling and mixed with a solution of acetate of lead, a yellow precipitate is formed (I.), which was washed with alcohol and dried at 212°. When an aqueous solution of neutral acetate of lead is heated to boiling, and the decoction of the coffee berries freed from fat added in small portions, a gelatinous, voluminous, pale yellow precipitate (II.) is formed, which was treated in the same manner as the first. A solution of acetate of lead produces, in a concentrated aqueous solution of the acid, a precipitate which at first is white, but on the addition of more acetate of lead becomes yellow (III.). The white precipitate melts at 212°, at first to a green oil, then solidifies and forms a green brittle resinous mass, containing 7 equivs. of the acid to 4 equivs. of the oxide of lead. The three lead salts above described possess the following composition:—

	I.			II.			III.		
Carbon.....	25·28	32	=25·35	24·73	32	=24·76	42·44	32	42·7
Hydrogen....	2·29	15	1·98	2·41	17	2·19	4·16	18	4·0
Oxygen.....	13·73	13	13·74	15·49	15	15·48	..	16	
Oxide of lead	58·70	4	58·93	57·37	4	57·37	..	1	

The author, moreover, succeeded accidentally in preparing two lead salts, one of which proved to be $C^{16} H^{8} O^{7} + PbO$, the other $C^{32} H^{15} O^{13} + 3PbO$.

The aqueous decoction of the coffee berries, after their extraction with æther, yields a precipitate with acetate of lead, which, after washing with water and decomposition with sulphuretted hydrogen, affords a yellowish solution, which, evaporated to the consistence of a syrup in the water-bath and mixed with alcohol, separates into two portions, one soluble, the other insoluble in alcohol. That soluble in alcohol behaves like a solution of the acid of coffee containing lime; it gives with acetate of lead a yellow precipitate containing variable quantities of oxide of lead, and is consequently a mixture of several lead salts. It was found impossible to obtain in this manner a lead salt of definite composition.

The different salts and the hydrate of the acid may be expressed by the following formula:—

$C^{16}H^{9}O^{8} = C^{16}H^{7}O^{6} + 2HO$

$C^{16}H^{8}O^{7}PbO = C^{16}H^{7}O^{6} + HO + PbO$

$C^{32}H^{15}O^{13}3PbO = C^{16}H^{7}O^{6} + 2PbO + C^{16}H^{7}O^{6} + PbO + HO$

$C^{32}H^{15}O^{13}4PbO = C^{16}H^{7}O^{6} + 2PbO + C^{16}H^{7}O^{6} + 2PbO + HO$

$C^{32}H^{17}O^{15}4PbO = C^{16}H^{7}O^{6} + 2PbO + C^{16}H^{7}O^{6} + 2PbO + 3HO$

$C^{32}H^{18}O^{16}BaO = C^{16}H^{7}O^{6} + 2HO + C^{16}H^{7}O^{6} + BaO + HO + HO$

Since the lead salts cannot be dried at a temperature above 212° without being considerably changed in appearance, it was impossible to attempt to expel the water, which does not act the part of base. The portion insoluble in alcohol, which remains after treating the aqueous extract with alcohol, contains little organic matter; this dissolves in water, and becomes brown when the aqueous solution is left exposed to the air for some hours. The analyses made with the lead precipitate gave the same relations between carbon and hydrogen, but different quantities of oxygen.

The composition of the substances contained in the coffee berries show a certain connexion to exist between them. They form, as it were, two series; to the one belongs the woody fibre, sugar, glycerine and oleic acid; to the second belongs the legumine, caffeine, the peculiar acid and palmitic acid. At all events, there is a certain connexion between them, and we shall undoubtedly succeed some day in discovering by means of accurate analysis the laws which prevail in the vegetable creation at the formation of the substances contained in plants.—Liebig's *Annalen*, lix. p. 300.

On the Seleniuret of Mercaptan. By C. Siemens.

Löwig obtained a seleniuret of ethyle by distilling the mixed solutions of seleniuret of potassium and sulphovinate of potash. He has not published any analysis of it. It was extremely probable that a seleniuret of mercaptan would likewise exist; that is to say, an alcohol with selenium in the place of oxygen or sulphur; this supposition has been fully confirmed by experiments made by the author, under the direction of Prof. Wöhler. Hydrated seleniuret of potassium (K Se + H Se) was prepared by saturating a solution of caustic potash with seleniuretted hydrogen gas in an apparatus into which at the same time hydrogen gas was passed to prevent the access of air. The solution of seleniuret thus obtained became immediately red by exposure to the air, and was therefore mixed as quickly as possible with a concentrated solution of sulphovinate of lime and submitted to distillation. At first seleniuretted hydrogen was set free, then water and a large quantity of a yellow liquid, which sank in the water with which it distilled over. This liquid, which is characterized by a most frightfully fœtid odour, was separated from the water, placed over chloride of calcium to dry it, and then again submitted to partial distillation, by which means it was separated into two liquids, one very volatile, the other distilling over at a

much higher temperature. The first is the seleniuret of mercaptan, the second the seleniuret of ethyle. The seleniuret of mercaptan is a colourless thin liquid, of an extremely disagreeable odour, resembling that of the cacodyle compounds; it is heavier than water, in which it is insoluble; its boiling-point is far below 212°; it takes fire readily, and burns with a very peculiar intense light-blue flame, diffusing dense white and red vapours of selenious acid and selenium. It combines with the oxide of mercury like the sulphuret of mercaptan with a hissing noise and great evolution of heat, to a yellow readily fusible body, which dissolves in hot alcohol, from which it separates in an amorphous state. An alcoholic solution of the seleniuret of mercaptan yields, with a solution of perchloride of mercury, a thick yellow precipitate. Its gas, passed through a glass tube at a faint red heat, is entirely decomposed with elimination of selenium. From this analogous behaviour to the sulphuret of mercaptan, there cannot be the least doubt that it is seleniuret of mercaptan with the formula $C^4 H^6 Se^2$, according to which it must contain 72·5 per cent. selenium. It could not be perfectly oxidized by nitric acid or chlorine, and an experiment with muriatic acid and chlorate of potash produced an explosion; it was therefore analysed by weighing off a portion in a small glass bulb, passing it in a gaseous state through a long weighed glass tube, which was filled at two places with short pieces of copper wire, where it was heated to faint redness. The gas was now so completely decomposed with the formation of very crystalline seleniuret of copper, that an odour only of benzole was perceptible at the open extremity, at the same time traces of carbon were deposited: 0·288 grm. gave, in this manner, 0·196 = 68·05 per cent. selenium. As it ought to have given 72·5, it is evident that it still contained some monoseleniuret of ethyle. The small quantity at the author's disposal did not admit of more accurate purification; for instance, by combining it with mercury. If it had been the monoseleniuret of ethyle = $C^4 H^5 Se$, it should have given 57·7 per cent. selenium; and had it been the biseleniuret of ethyle $C^4 H^5 Se^2$, it should have given 73 per cent. selenium.

The less volatile liquid which had been distilled from the seleniuret of mercaptan is either a mixture of this with the deutoseleniuret of ethyle, or a mixture of mono- and deuto- seleniuret of ethyle; it is a yellow liquid heavier than water, with an odour which is far more nauseous and lasting than that of the seleniuret of mercaptan; it burns like the latter, but oxide of mercury has no action upon it; it gave, on decomposition with incandescent copper, 63·73 per cent. selenium.—Liebig's *Annalen* for March.

On a Peculiar Change which Sugar experiences by the Action of Nitrosulphuric Acid. By C. F. Schönbein.

I have shown* that when sulphur, selenium, phosphorus and iodine are mixed with nitrosulphuric acid, they are rapidly oxidized

* See Chem. Gaz., p. 229 of the present volume.

even in the cold, and give rise to some curious reactions. The behaviour of cane-sugar towards the acid mixture in question is not less interesting. When 3 oz. of cold nitrosulphuric acid (consisting of 2 parts oil of vitriol and 1 part of chemically pure monohydrated nitric acid) are mixed with 1 oz. of finely-powdered cane-sugar, there is formed at first a thin transparent pasty mass. If it is stirred with a glass rod for a few minutes without interruption, the paste coagulates as it were, and separates from the liquid as a thick tenacious mass, aggregating into lumps, which can easily be removed from the acid mixture. Not a trace of gas is given off during this reaction, nor any vapours of hyponitric acid, but there is a slight development of heat. I may observe that the sugar does not experience this change when the acid mixture contains even a seventh of its weight of water.

If the lumps are immediately removed after their formation by means of a glass rod into cold water, they become hard; but in this state they may easily be drawn out like softened wax or resin. This substance smells strongly of hyponitric acid, has a very acid and intensely bitter taste, and weighs previously to being treated with water $\frac{3}{4}$ oz. Kneaded in warm water until the latter no longer reddens blue litmus-paper, it exhibits the following properties:— It is void of colour and smell, has a faint bitter taste something like mastic, is hard and brittle in the cold, may be rolled into forms like jalap-resin at the ordinary temperature, acquiring a silver colour and a beautiful silky lustre; it becomes soft and adhesive between the fingers, and may be drawn out into thin threads. It is perfectly insoluble in cold water, in which it sinks to the bottom, but melts in boiling water and is gradually dissolved, communicating to it a bitter taste. The solution remains clear on cooling, and has no action upon vegetable colours; when coloured blue by a solution of indigo and rendered slightly acid by sulphuric acid, it destroys the colour; the acidified solution also turns tincture of guaiacum and iodide of potassium paste blue, eliminates iodine from the iodide of potassium, converts the yellow prussiate into the red, and in a word behaves like the acidified solution of a nitrite. On evaporating the solution to which no acid has been added, it gradually becomes yellow, and leaves a brownish-yellow residue, which dissolves almost entirely in cold water, and possesses an extremely bitter taste. On heating the brown mass, it first puffs up and then explodes.

The substance dissolves in all proportions in æther at the ordinary temperature, yielding a colourless liquid, which on spontaneous evaporation leaves a transparent mass, which might be confounded with turpentine; it also dissolves readily in cold alcohol, and in fatty oils.

When the substance is cautiously heated in an open vessel to melting, it disengages aqueous vapour only; and if allowed to cool when no more water is given off, the residue appears transparent, nearly colourless, and strikingly resembles resin. If the application of heat is continued, it puffs up, giving off reddish-brown vapours

of hyponitric acid; if the mass is heated still stronger, it suddenly goes off like gunpowder, leaving but a slight trace of ash.

When the resinous substance is very gently heated with oil of vitriol, constantly stirring, it gradually dissolves without colour, and at the same time disengages a very penetrating acid odour like that of pure concentrated nitric acid. On mixing this solution with water, it disengages nitric oxide; it instantly destroys the colour of a solution of indigo, and in one respect behaves like a mixture of the so-called sulphate of nitric oxide with oil of vitriol. No precipitate is produced by water, however large a quantity be added, nor by a solution of potash, or of any other alkaline base. When the solution in oil of vitriol is heated, it is coloured brown, and fumes of hyponitric acid escape. It is remarkable that this solution has no bitter taste.

Concentrated nitric acid (1·5) dissolves the resinous substance in the cold without any evolution of gas. At 75° F. the solution is very rapid; and under these circumstances the substances may be mixed in every proportion, and solutions are obtained as thick and transparent as turpentine. When water is added to such a solution, the greater portion of the resin separates apparently unaltered; but the residuary liquid is acid and extremely bitter. If the acid anhydrous solution of resin is warmed gently, it becomes brownish-red, with evolution of hyponitric acid; and after this reaction, if the solution did not contain too much resin, it dissolves entirely in water and is no longer bitter. The resin dissolves in hot ordinary nitric acid, likewise with disengagement of red fumes: I have not yet succeeded in detecting oxalic acid in the residuary liquid.

A cold solution of potash, however concentrated, appears to have no action upon the resin at a moderate heat; however, it readily dissolves it, forming a dark brown liquid. On evaporating this to dryness, a brownish-black residue is obtained, which deflagrates when heated. The brown solution may be mixed with water in every proportion without producing a precipitate; acids do not render the liquid turbid, but decolorize it; excess of ammonia restores the brown colour. Oil of vitriol disengages hyponitric acid from the solution of the resin in concentrated potash. Nitrate and nitrite of potash are easily detected in the solution. When a piece of hydrate of potash is placed upon the resin melted in a platinum spoon, it froths up, instantly becomes brownish-black, and the entire mass takes fire a few instants after the reaction has commenced.

From the preceding facts, it is evident that the substance in question exhibits in many respects a great similarity to the resins, but essentially differs from them in others; it is, moreover, highly probable that the resinous substance contains hyponitric acid in intimate combination.

With respect to the acid mixture which is left on removing the resinous matter, it is thick, perfectly colourless, free from hyponitric acid or nitric oxide, and dissolves in water without any evolution of gas or elimination of a solid substance. The aqueous mixture not

only possesses an acid, but also an intensely bitter taste.—Poggendorff's *Annalen*, lxx. p. 100.

Chemical Examination of an Antique Blue Colour. *By* M. Girardin.

In a Roman bath discovered in the forest of Brotonne, near Routol, in the Départ. Seine Inférieure, a vessel was found containing several pounds of a blue pigment, which had certainly been in the form of a powder, but had become caked together from moisture. The colour is light blue, earthy, easily reduced to powder, tasteless, insoluble in water, but partially soluble in acids with effervescence. The insoluble portion is of a darker colour, rough to the touch, and is seen by a magnifier to consist of a pulverized vitreous substance. It is not altered by heating to redness, is not acted upon by acids, but may be decomposed by potash. The analysis of the powder yielded—

Silica	49·4
Alumina	6·4
Lime, with traces of magnesia and iron	19·4
Soda	15·5
Oxide of copper	9·3

This colouring material, which contains not a trace of cobalt, consequently corresponds to the *Cæruleum* of Vitruvius, of which Chaptal made an analysis in 1809. The ancients used this pigment to prepare all tints of blue by mixing it with chalk; it is for this reason that the different blue colours of the ancients, for instance the sky-blue examined by Delesse in 1842, differ principally by their amount of carbonate of lime.—*Journ. de Pharm. et de Chim*, x. p. 321.

On the Lactate of Lime. *By* Prof. Wackenroder.

The salt used for the experiments was obtained by saturating with carbonate of lime the lactic acid formed by the action of vegetable albumen upon milk-sugar. The salt, even as taken from the mother-ley, yielded not a trace of volatile organic acid on distillation with sulphuric acid; it was free therefore from any admixture of butyrate of lime. The occurrence of butyric acid, when milk is employed instead of albuminous vegetable juices, must consequently be referred to the fat of the milk, and not to the reaction of the nitrogenous substances upon the sugar.

If lactate of lime be exposed to a temperature of 176° it becomes soft, and loses a little water, and at 212° it melts in its water of crystallization; at 275° it parts with nearly the whole of its water, so that the smeary residuous mass experiences, even at 284°, but a slight loss in weight, not amounting to 1 per cent. Heated to 338°, there was still a loss of nearly $\frac{1}{2}$ per cent., and the weight of the water expelled amounted altogether to 29·167 per cent. However,

the water which escaped above 302° presented a slight acid reaction. Taking the formula for the lactate of lime $= CaO + C^6 H^5 O^5 + 5HO$, the whole of the water amounts to 29·050, which is but little exceeded by the quantity expelled up to 338°.

If the salt be dried in the air for some time at about 176°, it loses 20·47 per cent. in weight; if it be then further heated to 212° it no longer melts, and at this temperature only 2·51 per cent. more water is expelled, consequently altogether 22·98 per cent. Calculating the amount of water in 100 parts for 4 equivalents we find the number 23·56, which closely corresponds to that found by experiment. On heating the salt to above 338°, it loses from this temperature the 5th atom of water, and bears a temperature of 392° without any essential decomposition. The loss at 335° amounted to 28·969 per cent., and at 392° to 29·108. On drying lactate of lime at 212° until it has lost 15 per cent of water, and then heating it to 316°, it loses at this temperature all its water, viz. 29·305 per cent., which likewise exhibits a faint acid reaction.

If the salt be acted upon for some length of time by a temperature of 392°, it begins to melt slightly and to be decomposed. When heated with access of air, it melts to an amber-coloured gummy mass previously to being charred. On dry distillation an aromatic brown oil and an acid aqueous liquid were obtained, in which no acetic acid could be detected. The residue contained but little carbon. On heating the air-dried salt to redness, a residue was obtained which quickly burnt white, and which afforded 17·13 and 17·80 per cent. lime. These results, compared with those calculated from the formula, give,—

	Calculated.	Found.
CaO	18·39	17·80
$\overline{L}$	52·56	53·23
HO	5·81	5·99
4HO.....	23·24	22·98

Of this water 4 atoms escape on raising the temperature to 212°, the fifth, above 212°, and only entirely at 302°; it should therefore undoubtedly be regarded as saline water.

Pelouze's view, that lactide, $C^6 H^4 O^4$, which is formed by heating the hydrate of lactic acid to 302° with decomposition of a portion into carbonic acid and carbonic oxide, is contained in the anhydrous salts of lactic acid, does not well agree with the above results; for on heating the salt to 248° 1 atom of water should escape, while on the contrary the analyses of it, as well as those of the lactate of zinc dried at 212° and 338°, by E. Mitscherlich and Liebig, and which, according to Gay-Lussac and Pelouze, does not lose any more water, even at 473°, than in those analyses made at the above temperatures, agree with the formula MO, $C^6 H^5 O^5$. The observation that lactate of lime may be exposed to 257° without decomposition can be used to purify the lactate of lime, the other organic matters being destroyed.

In general the lactate of lime is obtained in the form of a light chalky mass, in which, however, with the aid of a magnifier, traces

of crystallization can be detected. When a very concentrated hot solution of the salt is allowed to cool slowly, the whole liquid solidifies to a crystalline mass; on slow spontaneous evaporation it is obtained in warty aggregations: 1 part of the air-dried salt requires 17·40 parts water for solution; boiling water dissolves an unlimited quantity, as at this temperature it melts in its water of crystallization. 3·26 parts to 1 part boiling water form a clear syrup, which becomes hard, brittle, and somewhat crystalline on cooling. The pure salt does not become mouldy, and is not deliquescent. It is scarcely soluble in alcohol of 0·83 spec. grav.; at 68° 1 part required 490 parts, but of boiling alcohol of the same strength only 1·216 part was required. The anhydrous salt does not dissolve even in boiling alcohol. From the hot solution of the hydrated salt in alcohol it crystallizes on cooling, and with a sufficient quantity the entire liquid solidifies. The salt is quite insoluble in æther of 0·728 spec. grav., and it can be precipitated in caseous flakes from the alcoholic solution by æther.

The hydrate of sulphuric acid dissolves the lactate of lime in the cold to a clear and colourless liquid, but on the application of heat the mixture becomes blackish brown, and among the gases disengaged sulphurous acid is perceptible. By fusing the salt with hydrate of potash a considerable quantity of oxalic acid is formed, together with acetic acid, without any gas being disengaged; it is probable that 7 atoms of oxygen are absorbed from the atmosphere, and the decomposition with reference to the lime salt may be represented by the following expression:—

$$2(CaO, C^6 H^5 O^5)$$
$$-CaO, C^2 O^3, \text{ which is nearly the proportion found,}$$
$$=\overline{CaO, C^{10} H^{10} O^7} + O^7$$
$$-(7CO^2, 4HO)$$
$$=\overline{CaO, C^8 H^6 O^6}.$$

So that in the residue acetic, oxalic, and carbonic acids are combined with potash and lime.

The solution of the lactate of lime in 10 parts of water is neutral, and remains clear. Solutions of most of the earthy and metallic salts produce no precipitation in it; sulphates only separate the whole of the lime as gypsum on boiling; protosulphate of iron and lactate of lime dissolved in equivalents in water, so that the entire quantity amounts to 10 parts, furnishing a very pure lactate of the protoxide of iron after separating the gypsum produced by boiling. The lactate of magnesia is, like the zinc salt, very characteristic; it falls in a crystalline state when a solution of the acetate is added to lactate of lime dissolved in 4 parts of water.—*Archiv der Pharm.* xlviii. p. 258.

On the Compounds of Phosphorus with Nitrogen. By M. Gerhardt.

Two compounds of phosphorus with nitrogen are known; the one PN^2 is obtained, according to H. Rose, by heating the ammoniacal

terchloride of phosphorus; and it may likewise be obtained, according to Wöhler and Liebig, from the ammoniacal compound of the pentachloride of phosphorus. The second combination was obtained by the latter chemists on treating the product of the reaction of ammonia upon the pentachloride of phosphorus with water, and was considered by them as a hydrate of the former, and received the formula PN^2 2HO. On treatment with potash these compounds yield ammonia and phosphoric acid, the formation of which upon the assumption of these formulæ appears to be very complicated, since for PN^2, HO or KO, to yield HO ammonia and phosphoric acid there is always wanting a quantity of hydrogen. According to the usual method of notation in equivalents,

$$PN^2 + 8HO + H = PO^5\ 3HO, 2NH^3.$$

According to Gerhardt's notation and his equivalents, in which PN and H represent the atom or the half equivalent, this expression assumes the following form,

$$PN^2, 4H^2O + H = PH^3O^4 + 2N H^3.$$

On the other hand, the behaviour of the chlorides of phosphorus towards ammonia is unusual, for hydrogen ought to be eliminated,

$$PCl^5 + 2NH^3 = PN^2 + 5HCl + H,$$

or a new and peculiar compound formed. The following experiments, which were made in consequence of these considerations, give a very different view respecting these compounds. When, for instance, dry ammoniacal gas is passed over pentachloride of phosphorus in a sufficiently wide glass tube, the ammonia is absorbed with evolution of considerable heat, and at the same time a quantity of muriatic acid is disengaged, which partly combines with ammonia, forming chloride of ammonium, which is deposited in the tube. Even the resulting product is mixed with chloride of ammonium, and cannot be obtained in an isolated state, for it is converted into the following compounds, both by washing and by heating it, in order to remove the chloride of ammonium. But from its mode of origin and these very reactions, the product mixed with chloride of ammonium, which mixture has hitherto been regarded as the ammoniochloride of phosphorus, must be chloro-phosphamide, with the composition $PCl^3 N^2 H^4$ according to the usual, and likewise Gerhardt's notation, since the expressions P, Cl, N, H in the former are all divisible by 2. If, after perfectly saturating the pentachloride of phosphorus with ammonia, the product is thrown into water, this very quickly acquires an acid reaction, owing to eliminated muriatic acid, and a large quantity of chloride of ammonium is dissolved. After long washing with hot water until no more muriatic acid is removed, a product is obtained, the purity of which is easily ascertained by heating it in a glass tube; no sublimate of chloride of ammonium should be formed. The purified residue forms in this state a white tasteless powder, and is a new body, phosphamide. To determine the amount of phosphorus in this compound, it was mixed with a small quantity of pure litharge;

the mixture moistened with nitric acid, and subsequently ignited, showed the amount of phosphoric acid absorbed by the increase in weight. The hydrogen was determined by an elementary analysis with oxide of copper, and the nitrogen by ignition with soda-lime. The results correspond to the formula $PH^3 N^2 O$ in Gerhardt's equivalents, or $PH^3 N^2 O^2$ according to the usual method. This formula differs in its constituents only by one additional equivalent of hydrogen, from that which the assumption of a hydrated phosphuret of nitrogen requires, according to the usual mode of notation PN^2, 2HO. The per-centage numbers of the formula for phosphamide, give with those resulting from analysis, the following comparison :—

P	40·4	40·5
H^3	3·9	3·8
N^2	35·0	35·4
O^2		20·3

When pure phosphamide is moistened and then heated rapidly in a test-tube to redness, it fuses, giving off a current of ammoniacal gas, and there is left a clear colourless glass of the hydrate of metaphosphoric acid, which soon absorbs moisture from the atmosphere and deliquesces. To produce this reaction, it is merely requisite to heat phosphamide which has been exposed to the air, it then contains the necessary quantity of moisture ; but if it has once been thoroughly dried it behaves in a very different manner. The above reaction will be readily explained from the following equation :—

$$PH^3, N^2 O^2 + 4HO = PO^5 + 2NH^3 + HO$$

phosphamide requires, consequently, in order to be converted into the sesquiphosphate of ammonia, the hydrogen and oxygen of 3 equivs. of water.

Solution of caustic potash does not act upon phosphamide, but potash in a state of fusion instantly produces tribasic phosphoric acid, with which it combines with disengagement of the simultaneously formed ammonia,

$$PH^3 N^2 O^2 + 3\,(KO, HO) = 3KO + PO^5 + 2NH^3.$$

The dry metaphosphoric acid must assimilate 3 equivs. water in order to pass into tribasic phosphoric acid ; phosphamide may therefore be accurately compared to it. Just as by heating the sesquiphosphate of ammonia 1 equiv. of ammonia is expelled and the acid salt formed, we obtain by heating phosphamide an analogous body, diphosphamide, $KOH^2 O$. It suffices to expose phosphamide for a long time to a faint red heat, protected from access of air, for instance, in a long glass tube, in order to expel half its nitrogen in the form of ammonia, and consequently the whole of its hydrogen. The residue is scarcely altered in appearance ; but the slightest trace of moisture causes the formation of phosphoric acid, which is immediately recognised by the melting of some particles. The analytical results led to the formula PNO^2 in ordinary equivalents.

P	50·8	51·6
N	22·4	22·6

This formula is confirmed by the reactions of this body; when moistened and raised rapidly to a red heat, it disengages ammonia with formation of metaphosphoric acid. Potash in a state of fusion liberates ammonia, and combines with tribasic phosphoric acid:

$$PNO^2 + 4HO = PO^5, HO + NH^3$$
$$PNO^2 + 3(KO, HO) = 3KO, PO^5 + NH^3$$

This amidogen compound is remarkable from its being the first in which a trace of hydrogen is no longer contained. The second amidogen compound, derived from the first, contains, like this, oxygen, and cannot be formed without the intervening reaction of water. The product, which is obtained when pentachloride of phosphorus perfectly saturated with ammonia is heated to redness, must consequently be very different from these amides. If it be heated to redness for a quarter of an hour, preventing the access of moisture as much as possible, the residue constitutes a new body, phospham, which, however, owing to the difficulty of carrying out the operation with perfectly dry material, is always contaminated with the two preceding products, according to the moisture and temperature, so that its composition could not be satisfactorily ascertained by analysis. But it must be observed, in order to judge of the composition of this body from its reactions, that the pentachloride of phosphorus and ammonia disengages, when heated, chloride of ammonium, and likewise free hydrochloric acid. If phospham be moistened with water and then quickly heated to redness, it disengages ammonia and leaves hydrated metaphosphoric acid; but this reaction can only be explained by assigning to phospham the formula PHN^2, for then we have

$$PHN^2 + 6HO = PO^5, HO + 2NH^3.$$

The connexion and formation of these three new bodies is explained in the following manner: since in the reaction of ammonia upon the pentachloride of phosphorus chloride of ammonium is disengaged along with free muriatic acid, the result cannot be merely a combination of ammonia with the perchloride of phosphorus, as generally assumed; an amidogen compound must result, which, as above stated, cannot be separated from the chloride of ammonium with which it is obtained mixed; but, judging from the three preceding bodies, it must be chlorophosphamide, $PCl^3 N^2 H^4$. The reaction is as follows:—

$$PCl^5 + 2NH^3 = PCl^3 N^2 H^4 + 2HCl.$$

Now this chlorophosphamide, mixed with chloride of ammonium, yields on treatment with water, muriatic acid and phosphamide,

$$PCl^3 N^2 H^4 + 2(HO) = PH^3 N^2 O^2 + 3HCl.$$

Phosphamide loses, when heated, half its nitrogen as ammonia, so that the whole of the hydrogen is removed from the residue. At a high temperature, and absence of moisture, the chlorophosphamide is

converted into phospham PHN^2 and muriatic acid, the intermixed chloride of ammonium escaping with the latter,

$$PCl^3\ N^2\ H^4 = PH\ N^2 + 3HCl.$$

All three compounds of phospham, phosphamide and diphosphamide, are converted by hydrate of potash in a state of fusion into tribasic phosphoric acid and ammonia, they are consequently the amides corresponding to the different modifications of phosphoric acid.—*Ann. de Chim. et de Phys.*, xviii. p. 188.

CHEMICAL PREPARATIONS.

On the Preparation of pure Barytic Water and pure Salts of Barytes. *By* H. Wackenroder.

When 240 grms. of finely-ground heavy spar are intimately mixed with 60 grms. of colophony and 20 grms. of powdered charcoal, and the mixture heated to redness in a covered crucible nearly filled with it, the sulphate of baryta is readily and advantageously decomposed. The ignition may be effected in an ordinary furnace of sheet iron provided with a dome, and is continued from half to three-quarters of an hour. When meal or sugar is employed for the reduction, and a very strong heat, approaching nearly to white heat, employed, soluble monosulphuret of barium is scarcely formed. The ignited mass is loose, yellowish-gray or reddish, and yields, on boiling with water in a porcelain dish, a saturated solution of baryta and bisulphuret of barium, together with some hyposulphite of baryta. The alkaline liquid is consequently yellowish, and deposits on suitable concentration a tolerable quantity of hydrate of baryta and some sulphuret of barium; the residue, insoluble in hot water, consists of undecomposed heavy spar with some coal, metallic sulphurets and the earthy substances mixed with the mineral and the coal. To prepare any salt of baryta, the sulphuret of barium is repeatedly exhausted with boiling rain-water, and the baryta precipitated by carbonate of soda. With very dilute nitric acid the solution readily yields perfectly pure nitrate of baryta, as this salt may be easily separated by crystallization from the less-easily crystallizing salts. Chemically-pure chloride of barium is most readily obtained. For this purpose, the solution is mixed with dilute crude muriatic acid until the liquid indicates the presence of a slight excess of acid; the precipitate of sulphur, sulphate of baryta, and at times also sulphuret of arsenic, is separated by filtration, and the liquid evaporated until but little mother-ley is left, which contains chloride of calcium, chloride of strontium and perchloride of iron. The dried chloride of barium is readily freed from adherent muriatic acid and perchloride of iron by exposure to a faint red heat, dissolving in water and filtering. About one-third the amount of the heavy spar employed is obtained; if the whole of the heavy spar had been reduced, a much larger quantity of chloride of barium would naturally be obtained, but the loss of heavy spar, which however may be em-

ployed in subsequent operations, is fully compensated for by the lesser amount of labour required.

To obtain perfectly pure barytic water, the sulphuret of barium is exhausted with as little boiling water as possible, and the yellow liquid allowed to cool in a tall covered glass. Upon this the liquid is separated as perfectly as possible from the crystallized hydrate of baryta; the latter then dissolved in water, and boiled in a porcelain dish with pure hydrated oxide of copper until a sample of the liquid yields with solution of acetate of lead a white precipitate. If, after boiling the liquid for some time, it is found to contain some copper, it is filtered, and a small quantity of hydrated oxide of silver or carbonate recently precipitated from the nitrate of silver by pure caustic or carbonate of soda, added to it. On digestion, every trace of hyposulphurous acid and oxide of copper is removed and sulphuret of silver formed.—*Archiv der Pharm.*, lviii. p. 171.

On a new Method of preparing Metaphosphate of Soda.
By Alexander Jamieson.

The conversion of the three modifications of phosphoric acid and its salts into one another, has hitherto been confined to the addition of free bases, or their removal by heat, when they were volatile. So far as I know, the reaction of salts upon each other, especially when heated, by which they would have the choice of taking up either the acid (or salt radical) or the base, and of thus forming some other modification, has not been studied.

I shall now communicate the result of an experiment which I made on this point at the suggestion of Prof. Liebig. The salt the reaction of which I studied was muriate of ammonia. Pyrophosphate of soda was prepared by rapidly heating to redness a mixture of the ordinary phosphate of soda, $PO^5, 2NaOHO, HO$, with an equal weight of muriate of ammonia. Ammonia was evolved; the fused mass, after driving off the excess of muriate of ammonia, when dissolved in water, possessed an acid reaction, and consisted of a mixture of metaphosphate of soda with chloride of sodium. By boiling the mass with alcohol diluted with an equal volume of water, I succeeded in separating the salts, the metaphosphate of soda remaining undissolved. The pure washed salt, after being dried, was fused in a platinum dish. It formed a beautiful clear glass, which deliqueseed in the air. For analysis, it was dissolved in water, and treated with neutral acetate of lead, whereby all the phosphoric acid was precipitated in combination with the oxide of lead. The filtered solution was treated with sulphuric acid to expel the acetic acid, and the soda estimated as sulphate. It yielded—

	I.	II.
Soda.....	29·9	30·1 per cent.

Equal equivalents of phosphoric acid and soda correspond to 30·4 per cent.

Thus, by the action of the chlorine, half the soda was extracted, whilst the acid passed into the monobasic modification.

If we heat a solution of pyrophosphate of soda with muriate of ammonia, ammonia is evolved; but no metaphosphate can be formed, because when this is heated with water, as is known, it becomes converted into pyrophosphate, and finally this into tribasic salt.—*Ann. der Pharm.*, lix. p. 350.

On a simple Method of preparing Corrosive Sublimate. *By* Drs A. *and* C. Walter.

The authors propose turning to account the property which chlorine-water possesses of converting calomel into corrosive sublimate, for the preparation of the latter. According to the method which they describe, calomel is prepared from the protonitrate of mercury and chloride of sodium, and is then placed in several separate vessels, as in the preparation of chlorate of potash, each of which must be capable of containing, without being quite filled, 8 parts of water for every 1 part of calomel placed in it. The gas is first passed through a washing trough, and then successively through all the vessels, until the whole is converted into a clear solution. The filtered solution is then evaporated and set aside to crystallize. Even with calomel, which had not been recently precipitated, the process proved perfectly successful. It would be highly advantageous if hot water could be employed instead of cold, and the vessels, with the exception of the last, heated upon a sand-bath; only 4 times the quantity of water would then be required, and a great part of the evaporation would be spared. Calomel may also be rubbed to a paste with water, and chlorine passed into it, when it also furnishes corrosive sublimate in the form of a crystalline powder.—Buch. *Rep.*, xliv. p. 35.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Adulteration of Wheat Flour. *By* M. Martens.

The following are the means proposed by the author for detecting the adulteration of wheat flour with the flour of potatoes and beans. It is known that potato starch is entirely insoluble in cold water when it has not been rubbed to a powder, so that the grains have remained entire; but if they are crushed in an agate or glass mortar, and water is then added, this dissolves a little of the starchy matter; and on filtering the mixture, after a few minutes' maceration in the cold, a clear liquid is obtained which is coloured blue by the addition of tincture of iodine; if pure wheat flour be treated in the same manner, the colour of the liquid is not altered, according to M. Martens, by the addition of iodized water, undoubtedly because the granules of wheaten starch are far more minute, and are enveloped in a coating of elastic gluten; they thus escape being

crushed by the pestle so as to expose the central portion which is capable of dissolving in cold water. M. Martens has found that a mixture of 5 per cent. of starch may be detected, if the flour be rubbed strongly for 5 or 10 minutes, with the precaution of triturating but little at a time.

Another adulteration, which is tolerably frequent, consists in mixing bean flour with wheaten flour. M. Martens' process for detecting this fraud, is based upon the presence of legumine in bean flour. The suspected flour is mixed with twice its volume of water, and allowed to macerate at a temperature of 68° to 86°, stirring from time to time; the whole is then poured on a filter, and washed with a little water to extract the whole of the legumine. If the filtered liquid contains any legumine, it becomes turbid and milky when a little acetic acid is very gradually added to it; it is also precipitated by the third hydrate of phosphoric acid. This process, which is very easily executed, enables us to detect the flour of beans or any other leguminous plant in that of wheat, even when the amount does not exceed 5 per cent.—*L'Institut*, Feb. 17, 1847.

On Artificial Blue Copper (Copper-Indigo).
By A. *and* C. Walter.

The monosulphuret of copper, hitherto artificially obtained either by precipitating persalts of copper with sulphuretted hydrogen or by treating the sesquisulphuret of copper with cold concentrated nitric acid, is generally not blue like copper-indigo, but dark green or brownish-black; if, however, the precipitate obtained with sulphuretted hydrogen is dried at a moderate temperature, it frequently yields a grayish-black powder, which under a steel polisher gives a faint steel-blue streak, especially when it is fixed by means of size upon paper, and after drying burnished with the polishing steel. According to the observations of Covelli respecting the formation of blue copper at Vesuvius, it appears as if it were produced by the long-continued action of sulphur upon persalts of copper; and the authors therefore attempted to prepare it in a similar manner. After numerous experiments, they found the following process to be the most advantageous:—Pure sulphate of copper is dissolved in hot water, dilute solution of caustic potash or soda added to it until nothing further is precipitated; the precipitate is then washed in hot water, and dried at a high temperature, until the entire mass has become converted into black oxide. 1 part of this oxide is now heated in an open dish with 1 part sulphur and ½ part chloride of ammonium until the sulphur takes fire; while the sulphur burns, the mixture is well-stirred, covered from time to time with a loose lid, removed from the fire for a time, and a fresh quantity of 1 part sulphur and ½ part chloride of ammonium added, the dish covered and again exposed to a gentle heat. When the dish has been left covered for some time, it is removed from the fire and allowed to cool and the lid taken off, when, if the right time has been hit, a portion of the sulphur will be found sublimed, and this should then

be furthered by gentle heat. If the mass does not possess a dark blue, but still a black colour, it must be mixed with more sulphur and chloride of ammonium, and heated as above, constantly taking care however that the temperature is not too high; it is on that account advisable to add from time to time fresh portions of powdered chloride of ammonium. The indigo-blue or dark black powder thus obtained is now finely ground, and washed with a sufficient quantity of water to remove all chloride of ammonium; to get rid entirely of the sulphur, the well-washed powder is boiled with a strong solution of potash or soda until no more sulphur is removed. It is frequently requisite to wash the compound, which has been well-exhausted with boiling ley, and to treat it with fresh ley. The mixture might also contain undecomposed oxide of copper, which could be removed by digestion with caustic ammonia, but not without occasioning some loss of sulphuret of copper. However, when the operation is well-conducted, especially with repeated additions of sulphur and chloride of ammonium, no such impurity will easily occur. The residuous mass is now well-washed with water, to remove all adherent potash and soda. The sulphuret of copper so obtained forms an indigo-blue or blackish blue dull powder, which when burnished with a polishing steel assumes a beautiful steel-blue tint. Ground up with oil or varnish, it affords a beautiful violet-blue. It can be prepared equally well from metallic copper, or by mixing the dry monosulphuret of copper with sulphur and chloride of ammonium, and treating it as above directed. Carbonate of copper would answer equally well, as also the nitrate, but not the chloride.

The compound described exhibits the same behaviour as the monosulphuret obtained by precipitating persalts of copper with sulphuretted hydrogen; but it is not dissolved so easily by cyanide of potassium or sulphuret of ammonium; but it dissolves readily in ammonia when air is allowed access, forming ammoniacal oxide of copper, and depositing sulphur. The authors have not yet made any analysis of this compound, but it is very probable that its composition is identical with that of blue copper. It is more difficult to answer the question whether it has the same composition as the bluish sulphur compound prepared by Winkelblech. The samples made by the authors, according to the method described by Winkelblech, did not possess the beautiful blue colour of the compound described.—Buch. *Rep.*, xliv. p. 14.

Experiments on the Detection and Quantitative Determination of Stearine and Stearic Acid in Wax. By E. Geith.

Carbonate of soda affords a ready method of detecting the adulteration of wax by stearic acid. When pure white or yellow wax is boiled in a porcelain dish with an equal weight of carbonate of soda and 6 parts of water, constantly stirring until a layer of carbonate of soda begins to form at the bottom of the dish, a tolerable quantity of the wax itself is saponified. If the mass, while still hot, is treated with

6 times the weight of the wax of alcohol of 0·80 spec. grav., and the whole then rubbed to a powder, with a gradual addition of from 16 to 18 parts of alcohol of 0·50 spec. grav., until the insoluble portion remains suspended in the liquid, a considerable precipitate is produced in the filtered solution by an acid. When, therefore, wax is tested with carbonate of soda for stearic acid, this substance saponifiable by soda must be previously extracted, which may be done with alcohol. In examining wax, it should first be tested for stearic acid; about 2 drms. of the sample to be examined are digested for some time in a flask with 1 oz. of lime-water and 1 oz. of distilled water, when the liquid, if stearic acid be present, loses its alkaline reaction. Regnault has, it is true, asserted that a precipitate of stearate of lime is deposited from the liquid, but the author was never able to obtain any such precipitate; on the contrary, even turbid lime-water became clear on digestion with the wax. When the absence of stearic acid has been thus ascertained, 1 drm. of the sample of wax is boiled for a few minutes in a flask with 2 oz. of alcohol of 0·80 spec. grav., and the whole poured into 1 oz. of alcohol of the same strength; after a few hours the finely-divided wax is collected on a filter, and washed with 2 oz. of the same alcohol. The wax on the filter is pressed between two porous tiles till nearly dry; it is then carefully transferred into a porcelain dish, and boiled with 1 drm. carbonate of soda and 6 drms. of distilled water, stirring the whole time, until some carbonate of soda begins to form on the bottom of the dish; 1 oz. of alcohol of 0·80 is added to the warm mass, and the mixture stirred gradually, adding some ounces of alcohol of 0·50, until the insoluble portion is converted into fine powder. When it has become perfectly cold, it is poured upon a filter, and edulcorated with alcohol of 0·50, until acetate of lead no longer produces any opacity; the whole is then evaporated to 1 oz. The residue is filtered when cold, and washed with weak spirit. The liquid which passes is well-shaken in a phial with 2 to 4 per cent. of stearic acid or stearine, a considerable froth is formed, which persists from half an hour to an hour; with pure wax the frothing is very slight, and it soon disappears. To further test the liquid, an excess of acetic acid is added to it; if the wax was pure, there is at the utmost only a faint opalescence; but if it contain stearine or stearic acid, a precipitate is formed, especially on shaking. If it is desired to determine the amount of these impurities, the liquid is not treated with acetic acid, but with acetate of lead, as long as a precipitate is formed, and the liquid then acidified with acetic acid. When the precipitate has subsided, it is collected on a weighed filter, and washed with distilled water until the liquid which passes through is no longer coloured by sulphuretted hydrogen. If the wax was pure, the quantity of the precipitate from 1 drm. only amounts from one-half to two-thirds of a grain; if it contained 10 per cent. stearine, it amounts to 2 to 2½ grs. The quantity of the precipitate is not constant, and it is far more easy to determine the stearic acid than the stearine, for with 5 per cent. of the former the precipitat e

amounts from 2 to $2\frac{2}{3}$ grs. M. Buchner states, in a note to the above paper, that he has convinced himself of the practicability of the above method.—Buch. *Rep.*, xliv. p. 153.

PATENT.

Patent granted to George Frederick Muntz, *Esq., M.P., for an Improved Manufacture of Metal Plates for Sheathing the Bottoms of Ships or other Vessels.*

This invention relates to the sheathing metal described in the specification of a patent granted to the present patentee, October 22, 1832, which metal is composed of copper and zinc, in such proportions, that, whilst the copper is to a considerable extent preserved, sufficient oxidation is produced, by the action of the sea-water on the metal, to keep the ship's bottom clean; 60 parts of copper are used in this mixture to 40 parts of zinc; and it has been found that this proportion of copper could not be reduced without exposing the alloy to injury, from the zinc being separately acted on. The present improvements consist in combining a suitable metal or metals with the copper and zinc, so that the mixture may contain a less proportion of copper than that above named; and at the same time a sufficient degree of oxidation may be produced, and a separate action on the zinc prevented.

The patentee describes an alloy of copper and zinc with another metal, which he has found to possess the same properties of oxidation as the metal described in his former specification, and yet with an important reduction in the quantity of copper employed, and consequently in the cost of producing the metal. The alloy consists of 56 parts of copper, $40\frac{3}{4}$ of zinc, and $3\frac{1}{4}$ of lead; and, in making the alloy, the patentee uses an additional quantity of zinc, on account of the loss of that material which occurs during the operation, so as to obtain an alloy containing the different metals in the above proportions. The lead is said to act a very important part in the alloy, as, without it, the combination of 56 parts of copper with $40\frac{3}{4}$ of zinc, would not produce an alloy which would oxidize sufficiently to keep the ship's bottom clean. The alloy, after being cast into ingots, is rolled into sheets (by preference, at a red heat), which are then to be annealed; and, if desired, the sheets may be cleaned with a mixture of sulphuric and nitric acids, properly diluted.

The patentee does not confine himself strictly to the above proportions, for the quantity of copper may be increased (which will, however, increase the cost of the sheathing metal), or it may be decreased to a slight extent; but it must not be reduced to 50 per cent. of the alloy produced. Although lead is mentioned in the above description, any other suitable metal may be used in place of it, but not with equal advantage.—Sealed October 15, 1846.

THE CHEMICAL GAZETTE.

No. CXIV.—July 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Formation of Chloral from Starch, and on a new Product of its Decomposition. By Dr. A. Stædeler.

We have already had occasion to notice that the author had succeeded in preparing chloral directly from starch*. The most advantageous method is to heat gently 1 part of starch with 7 parts of crude slightly-fuming muriatic acid, which should be as free as possible from sulphurous acid and diluted with an equal volume of water, until the pasty mass has become liquid; after cooling, 3 parts of manganese and some chloride of sodium are added, the latter to fix the sulphuric acid contained in the muriatic acid. The mixture is then distilled in a spacious flask, so as to attain the boiling-point as quickly as possible; the firing is then instantly removed; the mixture puffs up considerably, as in the preparation of formic acid from starch, manganese and sulphuric acid, with a violent evolution of carbonic acid, and continues to boil for some length of time. The mixture is kept constantly boiling, the distillate collected as long as a tolerably concentrated solution of potash produces in it any opacity, adding from time to time small portions of muriatic acid to it; and the distillation is discontinued when the presence of chloral can no longer be detected in the product either by its odour or by potash. At the commencement it carries over with it almost colourless oily drops, which are heavier than water, and possess an odour similar to the superchloride of formyle. They are separated from the remainder of the liquid, which is half-saturated with common salt. It is again submitted to distillation; the sulphur-coloured oil with an extremely acrid odour, formed at the commencement, separated from the distillate; and the same operation performed with the latter several times, in order to concentrate sufficiently the solution of chloral. The oily body is more quickly removed by supersaturating the distillate previously to each rectification with chalk than by mere partial distillation, as the chalk exerts on boiling a decomposing action on the oily body, but leaves the chloral unaltered. The concentrated solution is still coloured yellowish by an admixture of oil, and possesses the property of being rendered turbid by the addition of a few drops of water; however, this turbidness disappears by more water, and likewise on being warmed. It is supersaturated

* Vol. iii. p. 468.

with fused chloride of calcium, and lastly distilled from an oil-bath at 248°. The hydrate of chloral now passes over; it is colourless, and soon crystallizes to a white transparent mass. If the distillation proceeds slowly, the temperature is gradually increased; the hydrate of chloral which now passes over is coloured yellowish or brownish by a foreign substance, which likewise passes over with water in oily drops between 302° and 320°. This oil resembles in odour the sulphur-coloured one already mentioned; it is however distinct, and must not be mixed with it.

The impure hydrate of chloral thus obtained is mixed with 3 to 4 times its volume of sulphuric acid and gently warmed, when the chloral separates as a limpid stratum above the sulphuric acid, which becomes blackened, owing to the oily body being destroyed with evolution of muriatic acid. The separated chloral contains no other impurity besides hydrochloric acid, to expel which it is removed from the sulphuric acid, heated to boiling for some time, and, after having been again distilled over a small quantity of sulphuric acid, rectified over finely-divided perfectly-anhydrous caustic lime.

Chloralide.—When the hydrate of chloral is mixed with sulphuric acid, a considerable quantity is dissolved; and in placing the solution in a warmish spot, a disengagement of hydrochloric acid is perceived, and after some time the sulphuric acid becomes covered with a white body of crystalline appearance; if the mixture be allowed to stand for a longer time, the evolution of hydrochloric acid increases; and when it finally begins to cease, a quantity of very delicate shining acicular crystals are found to have separated in the sulphuric acid. This formation of crystals proceeds the more rapidly the more the mixture is warmed; and the best way of preparing this substance is the following:—The hydrate of chloral is mixed in a retort with from 4 to 6 vols. of pure sulphuric acid, and the two well-mixed at a gentle heat by shaking; the retort is then placed in an oil-bath, and the distillation carried on at a temperature of 248°–266° as long as chloral passes over. This is again converted into hydrate by the addition of a little water, and when the contents of the retort have become cold, returned to the sulphuric acid, intimately mixed with it by shaking, the chloral again distilled off at the stated temperature, and this operation repeated until at last the whole has become converted into the crystalline substance. When nothing more passes over between 248° and 266°, and the evolution of gas has nearly ceased, a limpid stratum is seen to rest upon the sulphuric acid, which, when the contents of the retort have cooled down to 212°, changes into a snowy-white crystalline crust, and usually the sides of the retort just above the sulphuric acid are covered with beautiful crystals. The perfectly cold mixture is then poured into a funnel stopped with asbestos; and when the sulphuric acid has drained off, the crystalline mass left for some time in contact with the air, when the still adherent sulphuric acid soon absorbs so much moisture that it can be washed with water without any fear of heating. As soon as the water no longer exhibits an acid reaction, the crystals are pressed between blotting-paper, placed upon a filter, and æther

poured upon them, which readily dissolves them. To the æthereal solution one-third of its volume of strong alcohol is added, and the whole then left to spontaneous evaporation, when crystals soon separate. However, this body, chloralide, is not the only product of decomposition of chloral by sulphuric acid; another liquid substance is formed at the same time, which tenaciously adheres to the crystals. By repeated crystallization it can be separated; and, on this account, the crystals which have separated from the mixture of æther and alcohol are removed from the mother-ley as soon as this has lost the æthereal odour, and are again dissolved in æther to which some alcohol has been added, and treated in the same manner several times, until they appear perfectly regular and quite hard, and melt between 234° and 237°.

Hydrated chloral appears to be requisite for the production of chloralide; none was formed on the rectification of the chloral which had been distilled from the sulphuric acid over a little sulphuric acid; on the contrary, nearly the whole of the chloral was re-obtained. Chloralide is insoluble in water and in sulphuric acid, and is not further altered by the latter. It dissolves sparingly in cold, but readily in boiling alcohol, as also in æther. From the hot saturated alcoholic solution it is deposited on cooling in very delicate, dazzling-white, microscopic crystals; from the mixture of æther and alcohol it separates in radiate groups of rectangular prisms, about 3 lines long and 1 line in diameter, with a simple oblique terminal surface. They belong to the clinorhombic system, are perfectly transparent, have a vitreous lustre and a remarkable cleavage parallel to the prismatic surfaces. Chloralide melts at 234° to 235°, and solidifies at 221° to 223°; it boils at 392°. When fused, it constitutes an oily liquid, which creeps up the sides of the flask, and there forms very delicate dendritic crystallizations. It has only a faint odour, but when heated its smell is extremely penetrating and pungent, not unlike that of chloral; from its insolubility in water it is nearly void of taste, but the alcoholic or æthereal solution has an acrid caustic taste. It burns with a highly luminous flame, the lower border of which is coloured green. No chlorine can be detected in the cold alcoholic solution by nitrate of silver; but when heated, a slight white turbidness results. If a drop of ammonia be added to the cold solution to which nitrate of silver has been added, a white precipitate of chloride of silver is formed, which readily dissolves in an excess of ammonia. Heated with an aqueous solution of potash, chloralide is immediately decomposed like chloral into superchloride of formyle and formiate of potash; when the alcoholic solution is treated with an alcoholic solution of potash, only formiate of potash and chloride of potassium are formed. Analysis gave—

	I.	II.	III.		
Carbon	18·74	18·55	19·28	5	18·61
Hydrogen	0·79	0·75	0·88	1	0·62
Chlorine	66·46	65·93	..	3	65·90
Oxygen	14·01	14·77	..	3	14·87

For I. and II. the chloralide was prepared from chloral from alcohol; for III. from starch; the latter, however, was not perfectly pure.

Chloralide has therefore the composition of chloral + 1 atom carbonic oxide. The rational formula is $2C^2\,HCl^3 + 3C^2\,O^2$; according to this it is a combination of 2 atoms of superchloride of formyle with 3 atoms of oxaloxide; the hypothetic oxide, which may be assumed to be combined with amidogen in oxamide. Chloral, $C^4\,HCl^3\,O^2$, may, on the contrary, be regarded as a combination of 1 equiv. oxaloxide with 1 equiv. superchloride of formyle $= C^2\,HCl^3 + C^2\,O^2$. The atomic weight of chloralide would therefore be twice as great as it is according to the empirical formula $C^5\,HCl^3\,O^3$; and, in fact, it must be doubled to explain the decomposition of this body by potash. 1 atom chloralide ($C^{10}\,H^2\,Cl^6\,O^6$) takes up 3 atoms of water, and then contains the elements of 3 atoms formic acid and 2 atoms superchloride of formyle. An aqueous solution of the potash combines only with the formic acid, eliminating the superchloride of formyle; but an alcoholic solution of potash also decomposes the superchloride of formyle formed, and so produces formiate of potash and chloride of potassium.

The second product formed along with the chloralide is an oily liquid, and lowers the melting-point of the chloralide to a considerable extent; in this case it melts even in hot water, and solidifies on cooling to a far less crystalline or even amorphous mass. The amount of carbon and hydrogen in this body must exceed that in chloralide. Two analyses of impure chloralide yielded 20 per cent. carbon and 0·9 per cent. hydrogen, consequently $1\frac{1}{2}$ per cent. carbon and $\frac{3}{10}$ths per cent. hydrogen more than should have been obtained according to the formula advanced. But if it is assumed that this body should not be regarded as an essential product of decomposition, the process of formation would be quite simply explained on the supposition that 4 atoms of chloral assimilate 4 atoms of water, and produce 1 atom of chloralide ($C^{10}\,H^2\,Cl^6\,O^6$), together with 6 atoms hydrochloric acid and 6 atoms carbonic oxide; and a portion of the latter being oxidized to carbonic acid at the expense of the sulphuric acid, gives rise to the simultaneous production of sulphurous acid. According to this, there should be disengaged a gaseous mixture of hydrochloric acid, carbonic oxide, carbonic acid and sulphurous acid.

Since it is very difficult to prepare pure chloral in small quantity, but very easy to obtain chloralide, it will certainly be advantageous, in determining the presence of chloral when it occurs in small quantity, to convert it into chloralide. For this purpose, the liquid in which chloral is suspected, after having been concentrated by distillation over chloride of calcium, is mixed with several volumes of sulphuric acid, and heated for some time to 248° to 266°. On cooling, it is mixed with from 5 to 6 vols. of water, when the carbonaceous matter, together with the chloralide, if any is present, subside to the bottom of the liquid. This is decanted, the sediment washed, dried between blotting-paper, and extracted with æther; the æthereal

solution leaves a very impure chloralide on evaporation. It is heated for some time with sulphuric acid, and the crystalline crust removed on cooling purified in the manner above described. If it is found impossible to obtain the chloralide perfectly white in this manner, it is submitted to distillation from an oil-bath most advantageously in a curved glass tube; the chloralide condenses in the long arm, and is perfectly pure after recrystallization.

The so-called insoluble chloral has, according to Liebig and Dumas, a different composition to chloral, while, according to a subsequent analysis of Regnault, it contains the same elements in the same proportion. The author has found the statement of Regnault to be perfectly correct, and there is no doubt that the insoluble and the soluble chloral are two isomeric bodies. Without doubt the chloral analysed by Liebig and Dumas contained an admixture of chloralide, the amount of carbon in which is higher and that of the chlorine smaller than in chloral, especially as the insoluble chloral prepared by them had been formed in the presence of sulphuric acid, by the action of which chloralide might have originated. The analyses of the insoluble chloral yielded—

	I.	II.		
Carbon.....	16·33	16·55	4	16·31
Hydrogen	0·89	0·98	1	0·68
Chlorine	71·54	71·54	3	72·16
Oxygen	11·24	10·93	2	10·85

The material employed for these analyses was obtained by mixing chloral with a little water; for I. it was exposed for a considerable length of time to a temperature of 212° to 248°, to remove every trace of adhering hydrate of chloral; for II. it was kept several days in water, then washed till it no longer exhibited any acid reaction, and dried over chloride of calcium.

Oily Products formed simultaneously with Chloral from Starch.—As above mentioned, some oily bodies and a resinous substance are formed under certain circumstances along with the chloral; but it appears that they may be all referred to one body, viz. the sulphur-yellow oil (α), which is obtained on rectifying the aqueous solution of chloral. This α oil makes its appearance, under all circumstances, among the products of the decomposition of starch and sugar by chlorine; it is the principal cause of the extremely pungent odour of the distillate, and with the above-mentioned proportions of starch, manganese and muriatic acid, is formed in less quantity than the chloral; but it is impossible to isolate the whole amount, as a great portion remains with the chloral, and can only be separated by destroying the latter. A greater amount is obtained when double the quantity of starch is taken, and the muriatic acid is diluted with $1\frac{1}{2}$ vol. of water. As soon as the distillate no longer possesses the pungent odour, muriatic acid or manganese is added, according as required, in small quantities, when each time effervescence occurs, and the distillate again presents the pungent odour; it is likewise necessary during the operation to take care that the mixture is suitably diluted, as this body experiences a decomposition when the

mixture is too concentrated, owing to the protochloride of manganese in solution, and the boiling-point is thereby raised too high, the oil α becoming mixed with the yellow oil β, which distils over between 302° and 320°, while iridescent globules are perceptible upon the products of distillation, and subsequently resinous masses are eliminated. The whole amount of the α oil is dissolved in the distillate; to obtain it, this, after the addition of common salt, is repeatedly distilled as long as oily drops separate at the commencement. The α oil is principally characterized by its being far more soluble when free from chloral in cold than in hot water; a cold saturated solution immediately becomes turbid when warmed, and at about 122° the greater portion of the oil separates in drops, the liquid again becoming clear. This affords an excellent method of separating it from any impurities; it is well-shaken with very cold water, the α oil separated from the clarified solution by warming, the residue treated with the same liquid in the above manner as long as any of the substance is separated by heat, and finally washed with hot water until litmus-paper is no longer reddened. In water it forms a clear sulphur-yellow oil, which sinks to the bottom and slowly changes its colour into a golden yellow. But when all the water perceptible is removed, the colour becomes darker, hydrochloric acid is eliminated, and the decomposition proceeds rapidly even in sealed glass tubes. If it is attempted to deprive it of water by means of chloride of calcium, it immediately becomes brown, resinous matters separate, and the portion of oil not decomposed has a strong acid reaction, due to the presence of free hydrochloric acid. It undergoes a similar though slower decomposition in dry air, and also under the air-pump; and the only plan of desiccating it for analysis is to leave it along with potash *in vacuo* until its colour begins to darken, when it is filled into little bulbs, and these sealed. But even in this way it cannot be dried perfectly, as it begins to turn brown after a few hours. The analysis of this oil gave 36·79 per cent. C, 3·09 H, and 47·59 Cl. These results agree, with the exception of the carbon, which is about 0·6 per cent. too high, with the formula $C^{18}H^{9}Cl^{4}O^{5}$; and although this formula cannot be correct, yet it shows that hydrogen, oxygen and chlorine are in the proportion to form water and muriatic acid; and if we consider a portion of the hydrogen, oxygen and chlorine as water and muriatic acid, which do not belong to the constitution of the body, then the amount of carbon would be increased in the same proportion. On this supposition, we find a very interesting relation to exist between this body and the so-called artificial oil of ants, the formation of which was first observed by Döbereiner in the preparation of formic acid from starch, manganese and sulphuric acid, and which was subsequently analysed by Stenhouse, and afterwards by Fownes. The former advanced the formula $C^{5}H^{2}O^{2}$ for this body; but the latter, who called it furfurol, considered that the formula should be trebled, as he prepared furfurolamide and furfurine from it, which could only be derived from the formula $C^{15}H^{6}O^{6}$. Now a very intimate connexion is seen to exist in the formation of furfurol and of the oil α; both ori-

ginate when a substance having great affinity for hydrogen acts upon starch; both are produced only in small quantity, together with formic acid and carbonic acid, and their properties likewise accord in many respects. Recently rectified furfurol is nearly colourless in contact with water; it becomes gradually yellow, but on depriving it of this it becomes even after a few hours brownish, and at last perfectly black. It dissolves in potash like the α oil, and acids separate from both solutions a brown resin. If we conceive half the oxygen in furfurol replaced by chlorine, we have a body, the composition of which would be expressed by the formula $C^{15} H^6 Cl^3 O^3$, and which would contain in 100 parts 39·79 carbon, 2·65 hydrogen, 46·97 chlorine, and 10·59 oxygen.

This calculated composition differs, it is true, considerably from that found; but if we assume that between 2 and 3 per cent. water and 1 per cent. hydrochloric acid were mixed with the analysed substance, these differences become much less; in fact, are such as not to exceed much the unavoidable errors of analysis. That during decomposition the amount of carbon is decreased, while that of the chlorine is increased, is proved by two accordant analyses, in which the oil had become so far decomposed while drying over sulphuric acid that a resinous body had separated in small patches, when it yielded 26 per cent. carbon and 66 per cent. chlorine.

The α oil is decomposed by sulphuric acid in the same manner as by chloride of calcium, into hydrochloric acid and a resinous body; but a portion of the latter is still further changed by the heat evolved with simultaneous elimination of carbon. Caustic potash and its carbonate produce a similar decomposition; but in this case the equivalents of Cl and H, which previously separated as hydrochloric acid, are fixed by the potash; chloride of potassium is formed, and the other elements are assimilated by the resinous body. Even on distilling the aqueous solution of this oil, a similar decomposition occurs to a smaller extent, as is perceptible from the acid reaction of the distillate, and from the colour of the liquid in the retort. It is more evident, however, when the oil is distilled with but little water; an apparently altered oil passes over along with a very acid water, and the residue consists of a thick brown liquid, from which on further heating the oil β is formed, while a tenacious resinous mass is left in the retort. This behaviour likewise explains the formation of the resinous body in the original mixture, which, with the last-stated proportions of starch, manganese and muriatic acid, is constantly produced if care be not constantly taken to keep the mixture sufficiently diluted. At first it is of very soft consistence; but if it has been kept long in contact with the boiling liquid, it becomes more solid, and its volume is diminished from β oil mixing with the α oil.

This resinous body dissolves in potash, and likewise in concentrated sulphuric acid, without any evolution of heat; it is separated from the former by acids, and from the latter by water, apparently in an unaltered state; it dissolves in alcohol and æther; on evaporation, the same amorphous resinous mass is obtained. It cannot

be dried, adheres very firmly to all objects touched by it, and burns with a luminous slightly green-margined flame, which may however arise from a small admixture of the α or β oil.

The β oil is a product of decomposition of the α oil, which it greatly resembles as regards colour and odour, but is distinguished from it by its colour becoming darker more quickly in the presence of chloral than is the case with the α oil, but principally by its behaviour towards water: while the α oil is more soluble in cold water, and may be separated by warming, the β oil dissolves readily in hot water, the solution becomes turbid on cooling, and finally a portion of the oil separates in drops. The oil γ, with an odour resembling that of the superchloride of formyle, is colourless, heavier than water, and appears to be very sparingly soluble in it. But it differs from the superchloride of formyle in its behaviour towards sulphuric acid, by which it is instantly converted into a black carbonaceous mass with evolution of hydrochloric acid. It is only formed when starch is acted upon by a large excess of chlorine, and not at all when an excess of starch is employed.—Liebig's *Annalen*, lxi. p. 101.

Action of Chlorine upon Citric Acid. By M. Plantamour.

Chlorine gas is absorbed very slowly by a concentrated solution of citric acid, but direct solar light somewhat accelerates the absorption. No carbonic acid is disengaged. The solution deposits a heavy oil (density 1·75 at 50°), boiling at 393°, and producing upon paper a greasy stain, which disappears in a few hours; it has a sweetish and hot taste, and a very irritating smell. M. Plantamour assigns to this oil the composition $C^8\,Cl^8\,O^3$ (no analytical details are given). Agitated with water and cooled to 43°, it crystallizes; the crystals are represented by the formula $C^8\,Cl^8\,O^3 + 3\,HO$; they fuse at 59°, giving off all their water at this temperature.

The action of chlorine upon the citrate of soda is quite different; it is very slow even when exposed to solar light, and carbonic acid is disengaged. The liquid becomes turbid and deposits an acrid oil, which is a mixture of several bodies; at the same time bicitrate of soda separates in acicular crystals.

M. Plantamour has not yet finished the investigation of the oily product; he has separated one substance which boils at 374°, which he represents by $C^5\,Cl^4\,O^2$. An alcoholic solution of potash produces with this oil, as well as with the first, $C^8\,Cl^8\,O^3$, chloride of potassium and some silky laminæ of a chlorinated potash salt containing $C^4\,Cl^3\,O^3\,KO$; the author calls the acid contained in it *bichloroxalic acid.*

The liquid in which the oil was deposited, after treating the citrate of soda with chlorine, still contains other products. When it is concentrated in a retort, an acid liquid and a little oil pass over. When the product is no longer acid the distillation is stopped; on saturating with carbonate of soda, crystals of the chloride are first obtained, and then an organic salt of soda, which on being precipitated

by nitrate of silver, yield a salt ($C^4 H^2 O^3 + AgO$) isomeric with the succinate of the same base. The author has named the acid contained in this salt *elaïloxalic acid.*—*Journ. de Pharm.* April.

On the Artificial Formation of Specular Iron. By T. S. Hunt.

The following is perhaps worth recording, as it beautifully confirms Mitscherlich's theory of the formation of this oxide in volcanic products. I precipitated a concentrated solution of perchloride of iron by caustic ammonia, and threw the thick magma upon a filter, where it was allowed to drain until it became solid. This was then partially dried at a gentle heat, when it cracked into small angular fragments. These consisted of hydrated peroxide of iron mechanically mixed with a large quantity of chloride of ammonium. On heating this in a platinum crucible to 400° or 500°, the vapours of water and the ammoniacal salt were abundantly disengaged, and the mass became inflated and porous. The residue however was not pure oxide of iron, for on heating it to bright redness, fumes of chloride of iron, accompanied by hydrochloric acid, were evolved, and an abundant deposit of dark red-brown oxide of iron coated the side of the crucible. On cooling, the oxide was found coated with a brilliant iridescence, which was still more beautifully seen in the small cavities disclosed on breaking the porous mass. A microscopic examination showed this coating to consist of small scales of specular oxide of iron, which exhibited all the splendid tints of the beautiful iridescent specimens from Elba.

The reaction which produced the specular iron is possibly the following:—A portion of the ammoniacal salt confined in the mass, which was half an inch in diameter, was unable to escape before the exterior became ignited. The heated oxide reacted upon the chloride of ammonium to form chloride of iron and water. Both of these bodies can probably exist undecomposed when in contact with oxide of iron, or at least the oxide and hydrochloric acid, if formed, would immediately react upon each other. But when they come to the surface the oxide is deposited and the hydrochloric acid escapes.—Silliman's *Journal*, November 1846.

Analysis of a Concretion from a Horse's Stomach.
By Dr. Boyé and Charles M. Wetherill.

This concretion is remarkable for its size, weighing $11\frac{3}{4}$ lbs. It is of an oval shape, smooth surface, brownish-gray colour, and breaks in concentric layers of different degrees of thickness, exhibiting a fibrous or radiated structure. The outer layer alone was analysed. The concretion was found, by Dr. Coates, to contain a nail in its centre.

By a qualitative examination, it was found to consist of phosphoric acid, magnesia, ammonia, chemically combined water, a small portion of organic matter, and silex. It contained no lime. In

order to determine quantitatively these ingredients, a portion was dissolved in dilute hydrochloric acid; the insoluble residue collected on a counterpoise filter, dried and weighed; after incineration and weighing, it yielded insoluble inorganic matter 0·45 per cent., which, deducted from its former weight, gives insoluble organic matter 0·64 per cent.

To the filtered solution was added a weighed portion of iron wire, dissolved in nitromuriatic acid, and the whole then precipitated by ammonia. Having previously ascertained the amount of peroxide of iron yielded by an equal portion of the same iron wire, the difference in weight of these two precipitates gave for the phosphoric acid, 32·40 per cent.

To the solution filtered from the phosphoric acid, was added caustic potash in excess, and the whole boiled until the ammoniacal vapours were effectually expelled, and the solution gave a strong alkaline reaction. The magnesia thus obtained was collected upon a filter, washed with boiling water, incinerated and weighed; it yielded magnesia, 14·45 per cent.

Another portion of the powdered concretion dried over sulphuric acid *in vacuo* at ordinary temperatures, yielded hygrometric moisture, 1 per cent.; incinerated, it yielded volatile matter (water and ammonia), 51·70 per cent.

In order to determine the amount of ammonia, another portion of the powder was introduced into a small tubulated retort, with carbonate of soda and water. The neck of the retort was adapted to a small tubulated receiver containing dilute hydrochloric acid, and having adapted to its tubulure a nitrogen bulb, such as is used in ultimate organic analysis; this also contained dilute hydrochloric acid. The mixture in the retort was evaporated to dryness; and at the close of the operation, air was drawn through the apparatus to ensure the absorption of the last portion of ammonia. The ammonia thus obtained was estimated by precipitation with chloride of platinum, as in organic analysis, and yielded 0·71 per cent.

Hence the composition of the concretion is as follows:—

Phosphoric acid	32·40	per cent.
Magnesia	14·45	...
Water	50·35	...
Ammonia	0·71	...
Insoluble inorganic matter	0·45	...
Insoluble organic matter	0·64	...
Hygroscopic moisture	1·00	...
	100·00	

It will be seen from this that the amount of ammonia is too small to be considered an essential ingredient of the concretion. Assuming it to exist in the state of double phosphate of ammonia and magnesia with water (NH^4O, $2MgO$, $PO^5 + 2HO + 10HO$), and deducting the amount of this salt from the rest (omitting the insoluble matter and hygroscopic moisture), it will be seen that the concretion is

composed mainly of the phosphate of magnesia and water, according to the following formula $3MgO + 3HO + 2PO^5 + 21$ aqua, as will be seen from the following comparison:—

Phosphoric acid	33·56	2 =	33·70
Magnesia	14·55	3	15·20
Water	51·89	24	51·10

Proc. of Amer. Phil. Soc. No. xxxv.

On the Precipitates formed by Caustic and Carbonated Alkalies in Solutions of Alum. *By* H. Bley.

When a solution of alum or of sulphate of alumina is precipitated in the cold by an insufficient quantity of caustic or carbonated alkali, or by an excess of caustic ammonia, a subsulphate of alumina is obtained. Berzelius assigns to the precipitate formed by ammonia in the neutral sulphate of alumina the formula $Al^2 O^3 SO^3 + 9HO$. According to the author, only mixtures are obtained according to the proportions of the reagent, whatever salt be employed, or whether it be precipitated hot or cold. The determinations of the alumina vary between 29·05 and 54·67 per cent., and those of the sulphuric acid to the same extent.—*Journ. für Prakt. Chem.*, xxix. p. 1.

On the Composition of the Root of the Radish. *By* Thornton J. Herapath.

The root of the common radish (*Raphanus sativus*) has been long known as an esculent; but this is the first time, as far as I am aware, that it has been subjected to a chemical examination. For this purpose, 1321 grs. of the fresh roots were taken, and scraped with a horn spatula, in order to separate the cortical part which contains the colouring matter. The scraped roots were then crushed to a pulp in a mortar, and repeatedly digested with cold water. The solution was passed through a muslin sieve; the pulpy mass remaining was then thrown on the sieve and subjected to pressure.

The solid matter remaining was boiled in water and filtered.

The residue, after treatment with cold and hot water, was boiled in alcohol and filtered. It was then boiled in diluted hydrochloric acid, washed, dried and weighed. It gave pure lignine, 22·58 grs.

A. The cold water solution, after remaining undisturbed for 24 hours, deposited a dark gray sediment, which was composed of a nitrogenous substance mixed with a little starch. It weighed 2·5 grs.

The opake solution, upon boiling, deposited 1·0 gr. of a dark-coloured albumen. The solution was then evaporated to a syrup, and treated with absolute alcohol boiling, until everything that was soluble in that menstruum was extracted.

The substances insoluble in alcohol were dissolved in water and evaporated to dryness; they were redissolved and evaporated several times successively, until the solution remained of a light amber

colour. 2·08 grs. of apotheme were left undissolved. The solution, upon evaporation, weighed 11·57 grs.

The alcoholic solution, upon evaporation to dryness, weighed 7·03 grs., which was composed of—

	grs.
Sugar	1·51
Extractive	0·5
Salts:—Nitrates of potash and soda, with a little chloride of potassium and sodium, and some acetates	5·02

The aqueous solution, upon evaporation to dryness, weighed 11·57 grs.; this was found to be composed of—

Extractive	0·4
Gum	5·68
Salts:—Chlorides of sodium and potassium, with a little nitrate	5·49

B. The hot water solution deposited a little of a nitrogenous substance on subsiding; this was collected and found to weigh ·2 gr. The solution was evaporated to dryness. The residue weighed 1·67 gr.

Alcohol extracted from it 0·67 gr., which was composed of—

Sugar	0·4
Acetates of potash, &c.	0·27

Water extracted 1·0 gr. It was composed of—

Gum	0·8
Nitrates of potash and soda	0·2

C. The alcoholic solution, upon evaporation, deposited some gamboge-coloured flocks. From the mass obtained upon evaporation, æther dissolved 0·53 gr. of an amber-coloured fixed oil, having rather a strong taste.

The remainder weighed 0·05 gr., and had a strong biting taste. There was not sufficient of it to enable me to ascertain its properties. It was probably sinapin.

D. The hydrochloric acid solution, upon testing, was found to be principally composed of the chlorides of calcium and magnesium, with a little sulphate of lime and the phosphates of magnesia and lime. Probably the chlorides existed as carbonates in the plant.

The rind was pounded in a mortar, and the pulp treated with equal parts of spirit and water, and passed through a sieve; the solid matter remaining was added to that from the fleshy part of the root.

	grs.
The solution, upon boiling, deposited a little albumen, which weighed	0·2
After boiling, it was evaporated to dryness, and weighed	3·97
From this alcohol extracted	1·609
Æther extracted	0·025

The colouring matter was left mixed with a small quantity of extractive, from which it was impossible to free it, as the colouring

matter was altered in its nature by repeated evaporations and solutions.

The colouring matter thus obtained was a purple uncrystallizable solid; it was turned to a carmine colour by the vegetable and diluted mineral acids. Ammonia and solutions of the fixed alkalies turned it to a rich green; as the excess of ammonia evaporated, it went through the various shades of green to a fine blue-green.

The colouring matter was insoluble in alcohol and æther, but was very soluble in weak spirit, and in water both hot and cold.

By repeated evaporations in contact with the air, at a temperature varying from 180° to 200° F., it was changed into a transparent body of a light brown colour, which was not altered either by acids or alkalies.

The alcoholic solution of the soluble salts from the rind was principally composed of the alkaline nitrates, with a little acetate of soda or potash.

The æther dissolved a small quantity of the acetates of soda or potash that had been left by the alcohol.

It will be seen from the preceding remarks, that 1321 grs. of the fresh radish root contains of—

Water	1267·820
Lignine	22·580
A nitrogenous substance, mixed with a little starch	2·700
Albumen	1·200
Extractive matter	2·980
Gum	5·680
Sugar	1·510
Purple-red colouring matter	2·336
Fixed oil	0·530
Sinapin?	0·050
Salts:—	
Carbonates and phosphates of lime and magnesia, with a little sulphate of lime	1·000
Acetates of potash and soda	0·295
Nitrates of potash and soda	6·829
Chlorides of potassium and sodium	5·490
	1321·000

In order to obtain the inorganic constituents, 875 grs. of the fresh roots were taken, dried and carbonized in a covered platinum crucible, as recommended by Professor Rose*, and the charred mass extracted with water. The carbonaceous mass remaining was dried and heated to redness over an Argand burner until a pure white ash was obtained; an excess of carbonate of ammonia was then added, and after evaporation to dryness it was slightly heated, so as to drive off the excess of carbonate, and extracted with water. The soluble salts obtained by the last experiment were added to those from the charred mass, and the solution evaporated to dryness; the residue weighed 5·22 grs.

* Chemical Gazette, No. 108.

The salts insoluble in water were dried, &c.; they weighed 2·03 grs.

These were found to contain, upon analysis—

Carbonate of soda	1·903
Carbonate of potash	1·971
Sulphate of soda	0·468
Chlorides of sodium and potassium	0·778
Carbonate of lime	0·500
Carbonate of magnesia	0·130
Sulphate of lime	0·010
Phosphate of lime	1·260
Phosphate of magnesia	0·100
Perphosphate of iron	0·010
Silica	0·020
	7·100

From the above it will be seen, that in 1000 parts of fresh roots there will be contained—

Water	959·742
Lignine	17·017
A nitrogenous substance, containing a little starch	2·043
Albumen	0·908
Extractive matter	2·261
Gum	4·299
Sugar	1·143
Purple-red colouring matter	1·768
Fixed oil	0·401
Sinapin?	0·037
Earthy phosphates and carbonates, with a little sulphate of lime	0·740
Acetates of potash and soda	0·223
Nitrates of potash and soda	5·169
Chlorides of potassium and sodium	4·155
	999·116

And, upon incineration, 1000 grs. would yield 8·285 grs. of ash; which would be composed of—

Carbonate of soda	2·174
Carbonate of potash	2·252
Sulphate of soda	0·534
Chlorides of sodium and potassium	0·889
Carbonate of lime	0·571
Carbonate of magnesia	0·148
Sulphate of lime	0·011
Phosphate of lime	1·440
Phosphate of magnesia	0·114
Perphosphate of iron	0·011
Silica	0·022
	8·166

On Fluorine and the Fluorides. *By* M. Louyet.

M. Louyet has repeated the experiments of Messrs. G. and Th. Knox on the means of isolating fluorine; most of the experiments were made in apparatus of Derby spar, which these gentlemen had placed at his disposal. He isolated the fluorine by decomposing fluorides, either by dry chlorine or by iodine which had been previously melted. It is a colourless odoriferous gas which does not bleach vegetable colours, decomposes water at the ordinary temperature, and has scarcely any action upon glass; it acts upon nearly all the metals, but not upon gold or platinum, except in the nascent state.

The fluoride of silver is a very deliquescent salt entirely decomposable by heat, and containing water in combination, which cannot be expelled without decomposing the salt; it therefore always yields acid vapours.

On treating the binoxide of mercury with hydrofluoric acid, a liquid is obtained which yields on evaporation a yellowish crystalline salt; when this is heated some acid is given off, and an oxyfluoride of mercury left. Sulphuric acid does not entirely decompose the fluoride of lead; according to M. Louyet, the compound $SO^3\,Pb\,O + 2Pb\,F^2$ is formed, upon which the acid has no further action.

M. Louyet has likewise determined the atomic weight of fluorine: 100 parts of very pure native fluoride of lime yielded 173·5 sulphate of lime, and 100 parts of the artificial fluoride gave 175·4; these numbers are each the mean of three experiments. According to Berzelius, 100 parts of the purest fluor spar yield 173·63 sulphate of lime. The author concludes from his experiments that the equivalent is 239·81, that is 19·18 times that of hydrogen. The analysis of the fluoride of lead led to the number 248·48. The author intends ascertaining the cause of these differences in another investigation, and concludes by calling attention to the necessity of taking the greatest precautions in preparing hydrofluoric acid, the vapours of which are extremely dangerous.—*Comptes Rendus*, xxiii. p. 960.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Artificial Gum. *By* M. Emile Thomas.

[Translated from the 'Bulletin de la Société d'Encouragement.']

During a lengthy stay in England, I had occasion to occupy myself with the manufacture of artificial gums. The facts which I collected, either from my own observations or from official communications, may, I trust, prove somewhat interesting to the Society of Encouragement, and I therefore hasten to communicate the same.

Since the discovery of diastase by Messrs. Payen and Persoz, and owing to the successful applications, made by the former of these gentlemen, of the various products from starch under the influence of that powerful reagent, a new discovery has been made in this branch of industry, viz. dextrine or artificial gum.

During the last two years especially the manufacture of dextrine has made immense progress in France, England and Germany. I will not here recapitulate the various uses to which this product may be advantageously applied; but I would observe, that the rapid development of a new branch of industry nearly always occasions, as in the present instance, the substitution of an œconomical product, of an easy and quick manufacture, for an expensive product, obtained by an uncertain manufacture.

In this case dextrine has replaced exotic gum for nearly all the purposes to which it was applied.

Dextrine is now met with in commerce in three distinct forms, viz. in the form of a white, brilliant and pearly powder; as a syrupy solution; and in the form of exotic gum, in greater or less perfection, either broken into small fragments, or made into rolls of various sizes.

Some short time ago, dextrine was only produced in the state of powder; and if some manufacturers have sought to give to it the appearance of the product for which it is to be substituted, they may have been induced to do so from the conviction that the only way to supersede the old plan was by humouring and even deceiving its disciples with the outward appearance of the new product. In this way our learned professor, M. Payen, who was formerly a manufacturer of some eminence, introduced borax of French manufacture, by giving it the dusty appearance of the Dutch crystals of borax, rounded and polished by the friction during their conveyance.

It has since been discovered that the gummy form of dextrine possessed many great advantages not at first contemplated. I shall allude to this presently, but would first observe, that there appears to be one disadvantage attending this form. Some intelligent persons were apprehensive that, taking advantage of the resemblance, exotic gum would be adulterated with artificial gum; fortunately this is impracticable, as the smell and taste of potato oil, which is always given out by artificial gum, are sufficient to betray its presence; and thus, if the purchaser suspects a fraud, he can easily detect it.

Dextrine may be manufactured either by the use of acids, or by means of the diastase contained in malted barley. I will examine these various processes in succession.

By Sulphuric Acid.—The dextrine produced possesses the disadvantageous property of being deliquescent, *i. e.* absorbing the humidity of the atmosphere. This method is therefore never employed, as, besides this disadvantage, the products are often coloured.

By Nitric Acid.—This method is now most generally followed for obtaining dextrine in the state of powder. I have thought proper to observe on this head, that the acid employed must be perfectly

pure, and for this reason—that nitric acid, as is well known, is obtained by the decomposition of nitrate of soda, obtained in the natural state from the coast of Bolivia, by means of sulphuric acid; now this salt always contains a portion of sea salt, which, together with the sulphuric acid and nitric acid, generates chlorine. Although but a small portion of this chlorine is contained in the acid, and consequently in much less proportion in the dextrine produced by that acid, it is nevertheless sufficient to considerably diminish the brilliancy and depth of the colours prepared with the dextrine. Several printers upon paper and fabrics have observed this, without being able to account for it otherwise than by attributing it to the inferior quality of the gum.

By Hydrochloric Acid.—This process is only employed to my knowledge by Messrs. Saint Etienne, who first renders the starch soluble, as in the former process, by means of a small dose of acid, and by torrefaction, or rather desiccation, at a high temperature.

The powder thus obtained is afterwards thrown upon a metallic sieve, and submitted to the action of a jet of steam, which damps the dextrine to such an extent as to render it transparent without liquefying it; so that it will require but very little drying afterwards. This process possesses the disadvantage of requiring great ability on the part of the workman charged with the hydration of the dextrine. The manipulation necessary for this operation is not acquired without great difficulty; so much so, indeed, that M. Saint Etienne, jun., who directs the working of his process in England, has not yet been able to find any person capable of undertaking this part of the work. Messrs. Saint Etienne prefer to use hydrochloric acid.

By Diastase.—This process seems the most worthy of attention in all respects; as, by adapting to it some modifications, which I have tried on a large scale, it will be found to be the one giving the most perfect results. I will therefore describe it fully.

The fecula must be rendered soluble in vats, heated by steam in such a manner that the temperature may be easily raised or lowered. The fecula is first mixed with 4 times its weight of water, previously heated to about 50°; for this purpose the fecula is gradually introduced into the vessel or boiler containing the hot water. In London, I employed copper boilers, with a double bottom, capable of containing about 400 gallons; and at one operation, about 600 lbs. of fecula, mixed with 1200 quarts of water, were decomposed. The temperature must be kept at about 60° until the whole mass is converted into starch; 2 per cent. by weight of very white malted barley is then added, and also the mucilage produced from 1 per cent. of linseed.

If a greater proportion of malt than that which I have mentioned were added, the decomposition would doubtless be more rapid; but a larger quantity of glucose would be formed, and the gum would be more coloured. With regard to the utility of the mucilage of linseed, it imparts tenacity to the gum. Instead of this substance I attempted to use lichen; but it did not answer, although the pro-

ducts were much whiter, by reason of the mucilage depositing itself upon the sides of the boiler, and preventing the liquid from boiling. It is, besides, not so strong as the linseed mucilage.

The mixture must be kept at a temperature of about 50° or 60° until all the starch is again dissolved; the temperature should then be suddenly raised, taking care however not to exceed 75° C., but keeping as near that temperature as possible, in order to cause the diastase to act as powerfully as possible. It will then be necessary to stir the mixture well until the decomposition is almost complete; this may be ascertained by the deep blue tint the mixture assumes, and by the action of the solution of iodine, which in that case will colour the dextrine of a violet, approaching to red, without any mixture of blue.

It is unnecessary to say, that, during the decomposition, the liquid must be kept constantly in motion. The operation lasts about an hour and a quarter; that is to say, a quarter of an hour for the formation of the paste, one for its dissolution, and the other three-quarters for rendering it soluble.

I much prefer this method of forming the paste to adding the malt, as the reagent spreads much more uniformly throughout the mass, and does not at once fall to the bottom of the vessel in which the operation is performed.

The liquor must now be removed from the decomposing vats, and left in pans to settle for from 6 to 18 hours, according to the external temperature. During this time a slight fermentation will be perceptible, but it must be checked by adding alum in the proportion of 10 grms. for every 25 gallons of liquid. It is essential to allow this time for the mixture to settle, as it prevents two serious evils; viz. the colouring of the gum while baking, and a singular phænomenon so often observed in evaporating viscous liquids, viz. their being quite still, and which I have ascertained is caused by the formation of a very thick sediment on the sides of the evaporating vessels.

The liquor, when drawn off after settling, will mark about 10° B., and it is evaporated by raising it very slowly to the boiling-point; which precaution is indispensable, for the perfect clarification is accelerated by checking the first boiling, as in refining sugar. This clarification is effected without any foreign agent, by the coagulation of the vegetable albumen contained in the malt and the linseed mucilage. As scum will continue to rise to the top of the mucilaginous syrup during most of the time of baking, it will be necessary to remove it carefully; and if the boiling is too much accelerated, the gum will first become thick, and afterwards will be coloured. When a solid pellicle of gum is formed at the surface of the syrup, the baking will be completed, at which time the syrup will mark about 35° B.

If it be desired to keep the gum in a liquid form, the baking must be stopped at 30° while boiling; the syrup must then be poured into well-closed vessels, previously rubbed with oil of turpentine, and the surface of the gum covered with a thin layer of that oil.

This method succeeded pretty well for preventing the fermentation of the liquid gum.

When it is desired to solidify the gum, the boiling syrup is poured into small flat tin vessels, placed upon a hot air stove, kept at a temperature of from 40° to 50° C. At the end of 24 hours the gum will acquire the consistency of jujube paste; it is then cut up into small oblong pieces with a pair of shears, and these pieces are rolled out upon a polished table, with a wooden roller, dusted with pulverized artificial gum, and afterwards placed upon wooden frames, and left for three or four days to dry. The gum would be much better dried by letting the syrup run upon a cylinder heated to 110° or 120°; but the œconomy of this process is questionable. The artificial gum thus prepared is easily dissolved, and makes a very clear solution; over dextrine, in the state of powder, it possesses the advantage of being more readily packed; and over liquid gum, the advantage of not fermenting.

The experiments which I have made with the various products of starch have led me to other inquiries upon analogous substances, and principally upon ligneous fibre and cellular tissue, which, as is well known, according to the experiments of M. Payen, are of the same composition as starch. At a future meeting I hope to communicate to the Society the results of some experiments upon the steeping of textile fibres, by means of processes analogous to those employed in manufacturing dextrine or sugar.

I will conclude by some observations upon an improvement which may be introduced in the manufacture of starch by washing. In the manufactory at Habertonford Mills, in the county of Devon, where M. Saint Etienne is superintendent, he is occupied in the production of starch by M. E. Martin's process, which consists, as is well known, in washing the paste obtained by means of wheaten flour under the action of a current of water and a mechanical softener. For this process it is essential that flour may be easily procured. Not having this facility, M. Saint Etienne conceived the idea of steeping the grain whole in water for two or three days, and then crushing it between rollers, and thus forming the paste. But this method was attended with a serious evil, viz. that the starch was not deposited, especially in summer. M. Saint Etienne attributed this to the quality of the water, but I convinced him that it was owing to the fermentation and partial germination of the corn, which being so long in contact with the water formed successively diastase and dextrine, and thus rendered the water which was used for washing the starch viscous. At my suggestion, he constructed an apparatus of wood, lined with lead, and having filled it three parts full of corn, he then added water sufficient to cover it. This apparatus was submitted to a constant heat of 50° C. as the maximum, with a pressure of from 15 to 20 atmospheres, and in four or five hours the grain swelled so as to completely fill the apparatus. A great quantity of water being thus absorbed, a paste could easily be formed by passing it between wooden rollers. Paste thus obtained may be used for making starch, care being taken to leave it

to settle for two hours longer than the paste made with flour, before softening it; there is then less fear of fermentation, and about 10 per cent. more available paste will be obtained than by grinding.—Newton's *London Journal*, No. clxxix.

PATENT.

Patent granted to Maximilian François Joseph Delfosse, *for Improvements in Preventing and Removing Incrustation in Steam-Boilers.*

This invention consists in preventing and removing incrustations in steam-boilers by the addition to the water used therein of a certain mixture which acts on the precipitable matters contained in the water in such a manner as to prevent their forming any incrustations on the interior of the boiler, and which will also remove any incrustations that may have been previously formed.

The mixture is termed by the patentee the "antipetrifying mixture;" the materials composing it are, first, dry tannic or gallic extract, obtained from the bark of oak and other trees, or from gall-nuts or roots, or from any other substances containing the same; secondly, hydrate of soda, or soda deprived of its carbonic acid; thirdly, muriate of soda; and fourthly, subcarbonate of potash. The proportions in which these ingredients are used, and the quantity of the mixture employed, will vary with the greater or less impurity of the water, and according as the boiler is stationary or locomotive. If the boiler is a stationary one, and it is fed with fresh water, the amount of antipetrifying mixture required for 336 hours' consumption per horse-power may be made by mixing together 12 ounces of muriate of soda, $2\frac{1}{2}$ ounces of hydrate of soda, 2 drachms of the dry tannic or gallic extract, and $\frac{1}{2}$ ounce of subcarbonate of potash: for locomotive boilers, travelling on an average about 140 miles each day, the quantity of the mixture per horse-power is increased one-fifth. If the water should be brackish, or a mixture of salt water and fresh (such as the water of tidal rivers), the patentee omits the muriate of soda, and uses 6 ounces instead of $2\frac{1}{2}$ of hydrate of soda, and 5 drachms instead of 2 of the dry tannic or gallic extract; the mixture is also prepared in this manner when sea-water is used in the boiler. The patentee prefers to introduce the mixture into stationary boilers in quantities sufficient for two, three, or more days; but locomotive and marine boilers are to be supplied daily with a portion of the mixture, corresponding with the amount of duty to be performed. The mixture may be introduced into the boilers of stationary engines, and into either the feed-tanks or boilers of marine engines; but for locomotive engines it is better to add a portion daily to the water in the tender.—Sealed August 25, 1846.

THE CHEMICAL GAZETTE.

No. CXV.—August 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Presence of Arsenic and Phosphorus in Iron.

By Dr. SCHAFHAEUTL.

THE repeated detection of arsenic in iron ores by Prof. Walchner has created much surprise (although it was previously known that most iron ores contained arsenic), and ultimately led to its discovery even in deposits from mineral waters. During my travels in England, France and Spain in 1833–42, I analysed most kinds of the iron ores, cast iron, bar iron and steel of these countries, and seldom found arsenic, antimony, tin and phosphorus absent.

In 1839 the results of my investigations were laid before the British Association at Birmingham; and in the same year a paper was published in the London and Edinburgh Philosophical Magazine (vols. xv. and xvi.), in which I showed that arsenic was present in the Swedish iron and the English Low-Moor iron; that on forging the best cast steel (made from Dannemora iron), the arsenic was volatilized, becoming recognizable by its odour, and frequently producing swelling of the lips in the workmen; that its presence was the cause of the Low-Moor iron excelling all other English iron in hardness and ductility. I have found out a method of artificially making iron so as to resemble this, and which is applicable to the manufacture of the same steel for which it is used. This will be described under the article "Steel" in the next volume which appears of Prechtl's 'Technological Encyclopædia.' Phosphorus is as frequently found in iron ores as in the cast iron prepared from them. It has hitherto been very frequently overlooked, because in many kinds of iron the greater part of it escapes during the solution of the iron in muriatic acid, as phosphuretted hydrogen and a gaseous compound, the nature of which is unknown, but which is neither decomposed by mercurial nor silver salts. By the following method, these gaseous compounds, &c. may be simply and directly determined.

A small glass tube, about 3 inches long, is inserted into the perforated cork stopper of an ordinary gas bottle; it must be somewhat contracted anteriorly at the point, like an ordinary washing bottle. This tube serves as a burner for the escaping hydrogen. But it must be bent laterally beyond the stopper at about one-third of its length, so as to form an angle of about 25°–30° with the horizon.

A glass tube, open at both ends, about 12 inches long and ½ an

inch wide, is now fixed in the same direction, and so that its lower aperture is at most a line distant from that of the burner. A small porcelain crucible is placed beneath its lower extremity.

The bottle is then filled with very dilute muriatic acid, as much as possible, without fear of the fluid running over; the coarsely bruised iron for examination is then added; and when the greater part of the air is expelled from the bottle, the jet of gas inflamed. As soon as the flame of the burning hydrogen gas is brought near the lower aperture of the above-described inclined tube, a current of air is formed in it, whereby the flame is for the most part drawn in; all those products of combustion which are not volatile, together with the water produced, &c., condense and collect in the inclined tube, and then run down into the capsule placed beneath it. A portion of the phosphoric acid produced is usually deposited in the solid form at the lower part of the red-hot mouth of the tube; and it is worthy of remark, that in this way as accurate a quantitative result may generally be obtained as when the gas is conducted over red-hot chloride or sulphuret of copper. By inclining the tube more or less, the draught of air may be more or less increased.—*Journ. für Prakt. Chem.*, 1847, No. 5.

On the Action of Chlorine upon Aqueous Prussic Acid. *By* Ad. Wurtz.

When a current of chlorine is passed into aqueous prussic acid, prepared by the process of M. Trautwein, the reaction which ensues produces in the course of a short time a slight elevation of temperature. The liquid gives off a very decided odour of chloride of cyanogen, and disengages a vapour which condenses into drops in the cold parts of the apparatus, and which constitutes the principal product of this reaction. In order to collect it, the retort containing the prussic acid is adapted to a chloride of calcium tube, which terminates in a tube curved at a right angle, and which is inserted into a long-necked flask, kept cool by means of ice. At the end of the operation the receiver contains a very volatile, limpid liquid, which fumes on exposure to the air, and diffuses a very irritating odour of chloride of cyanogen; it is the impure chlorohydruret of cyanogen. It contains hydrochloric and hydrocyanic acid, which are removed by agitating it with from 2 to 3 times its volume of cold water. The stratum of liquid which separates from the water is decanted and submitted to distillation, passing the vapour through a tube containing chloride of calcium.

The chlorohydruret of cyanogen thus prepared is a colourless, very fluid and highly corrosive liquid. It diffuses an odour which greatly irritates the nostrils, and especially the eyes, causing an abundant flow of tears; it boils at 68° F.; its vapour burns with a violet flame. It dissolves somewhat in water, and this solution gives a white precipitate with nitrate of silver. Placed in contact with dry chlorine, it is converted entirely into solid chloride of cyanogen and hydrochloric acid. When this reaction is made with several grammes

of substance, the sides of the vessel are seen to become covered in the course of a day with beautiful radiated needles, at the same time that a viscous liquid remains at the bottom, which subsequently solidifies entirely into large crystals of the solid chloride of cyanogen.

I found some difficulty in analysing the chlorohydruret of cyanogen, which will readily be conceived considering the extreme volatility of the liquid. The analyses which I have made lead to the formula $C^6 N^3 Cl^2 H$, which moreover appears justified by the reactions which the substance exhibits. It may therefore be viewed as a combination of prussic acid with the chloride of cyanogen, $C^4 N^2 Cl^2$, which will be described further on, or as a solid chloride of cyanogen, in which 1 equiv. of chlorine is replaced by 1 equiv. of hydrogen.

Liquid Chloride of Cyanogen.—To prepare this body, the chlorohydruret of cyanogen is treated with red oxide of mercury. To avoid too violent a reaction, it is best to mix the oxide with fused and powdered chloride of calcium, and to cool the mixture. After some hours' contact it is distilled in a water-bath, when a colourless liquid, which constitutes a new modification of the chloride of cyanogen, is seen to condense in the recipient, which should be kept sufficiently cool. It forms a limpid liquid, which, like the chlorohydruret, violently irritates the mucous membrane of the nostrils, and occasions a flow of tears; it is heavier than water, boils at 60°, and solidifies at 19° into a crystalline mass of long transparent laminæ. Its vapour is incombustible. It falls to the bottom of water, dissolving however slightly; this solution does not precipitate nitrate of silver. When a drop of potash is added to it, and it is then neutralized with nitric acid, there is an effervescence of carbonic acid, and the neutralized liquid yields a precipitate with nitrate of silver. These reactions appear to indicate that alkalies decompose the chloride of cyanogen into alkaline chloride, ammonia and carbonic acid; the two last products are known to be products of the decomposition of cyanic acid. The analyses which I have made of the liquid chloride of cyanogen lead to the formula $C^4 N^2 Cl^2$.—*Comptes Rendus*, March 15, 1847.

Chemical Examination of the Yolk of Egg. *By* M. Gobley.

The following are the conclusions which the author draws from experiments made since the publication of his former paper upon this subject*:—

1. The fatty matter of the yolk of egg consists, as previously stated, of two distinct portions, a fixed oil, *egg-oil*, and a soft infusible substance, the *viscous matter*.

2. The phosphorus occurs in the viscous substance, but not in the oil.

3. The oleic, margaric, phosphoglyceric and lactic acids, and the extract of meat, are not products of oxidation.

* Chem. Gaz., vol. iii. pp. 443, 486.

4. The viscous substance is not, as previously supposed by the author, a compound of oleic, margaric and phosphoglyceric acids with ammonia, but constitutes a body of very complex nature, from which the author has already separated two distinct substances, which he has called provisionally *phosphorized substance* and *cerebric substance.*

5. The phosphorized substance, which forms in the developed animal the body which is called oleophosphoric acid by M. Fremy, yields with the greatest ease, oleic, margaric and phosphoglyceric acids, as products of decomposition by mineral acids and alkalies, in the presence of water as well as of alcohol, and without the intervention of the oxygen of the atmosphere.

6. The cerebric substance is analogous, if not identical with the body which Vauquelin, Couerbe and Fremy have successively called by the names of fatty substance of the brain, cerebrote and cerebric acid.—*Comptes Rendus*, April 12, 1847.

Observations on the Hydrated Peroxide of Iron and Magnesia as Antidotes in Cases of Poisoning by Arsenic. By E. Riegel.

It is stated by M. Guibourt, that in order to precipitate 1 part of arsenious acid, 6·67 parts of dry peroxide of iron in the form of hydrate would not be quite sufficient. The author was also able to detect arsenic in the filtered solution by sulphuretted hydrogen, whenever the quantity of the oxide added amounted to less than 7 parts; with more than 7 and less than 10 parts, mere traces could be found by Marsh's test; and with more than 10 parts the liquid was perfectly free from it. The arsenite of the peroxide of iron formed is blackish-brown, heavy, and parts with water and a portion of the acid when heated in a little glass bulb. With arsenic acid at least 12 parts of oxide must be used in order to precipitate the acid completely. When the arsenious acid is not free, but combined with an alkali, it is not entirely precipitated by the hydrated oxide of iron, on which account Duflos recommended the peracetate of iron; but for this to effect its object, it should contain a certain quantity of hydrated peroxide mixed with it; however, the precipitate obtained with arsenious acid from the peracetate of iron is not, as stated by Bunsen, quite insoluble in acetic acid. With regard to the hydrate of magnesia, which has been recommended by Bussy as an antidote in cases of poisoning by arsenic, the author has confirmed the statements of that chemist; but he considers the preparation in the moist way to be more advantageous than that proposed by him. To precipitate entirely 1 part of arsenious acid, about 18 parts of anhydrous magnesia are required; when a less quantity is employed, there is always left in the liquid a larger or smaller amount of arsenic. The author recommends precipitating 100 parts of crystallized sulphate of magnesia with 50 parts of caustic potash, well washing the precipitate, and then submitting it to pressure in linen, and preserving it under water in stoppered bottles. The combination of arsenious acid with magnesia the author found to be perfectly insoluble in cold and

boiling water. When the arsenious acid was combined with alkalies, it was not completely precipitated by magnesia; however, better results were obtained by mixing undecomposed magnesian salt with the hydrate of magnesia; on which account the author recommends a mixture of equal parts of hydrate of magnesia and sulphate in water as the most advantageous form, especially as it is uncertain whether the poisoning has resulted from free arsenious acid or an alkaline arsenite. The author observes, in conclusion, that the basic ammonio-arseniate of magnesia, described by Levol as a new compound*, had already been prepared by Wach.—*Jahrb. für Prakt. Pharm.*, xiii. p. 390.

On Crystalline Slags. By J. Percy, M.D. F.R.S.

In the report presented to the meeting of the British Association held at Southampton in September 1846, and from which the following remarks are abstracted, the author confines his attention to the slags produced in the smelting and manufacture of iron.

The crystallographic and mineral descriptions are by Prof. Miller, most of the analyses were made by Dr. Percy, the remainder by Mr. David Forbes.

The first five slags were crystallized in square prisms, terminated by planes perpendicular to the axis of the prism; many of the prisms having their angles truncated by planes making equal angles with the adjacent faces of the prism. On analysis the first series (6) were found to contain silica, alumina, lime, magnesia, protoxides of manganese and iron, potash in small quantity, and sulphur as sulphuret. Phosphoric acid was also found in some of them. They are readily decomposed by digestion with dilute hydrochloric acid. The following method of analysis was adopted.

1. The fine powder obtained by trituration was digested with dilute hydrochloric acid. The whole was evaporated to dryness. The dry mass was treated with hydrochloric acid, and left for a few hours. Nitric acid was added sometimes before and sometimes after evaporation to peroxidize the iron. The silica separated by filtration was washed with boiling water until nitrate of silver ceased to produce the slightest turbidity, dried, incinerated at a bright red heat, and then weighed.

2. To the acid solution a slight excess of ammonia was added. Filtration was conducted as rapidly as possible, the funnel being covered with a glass plate.

3. The precipitate (2) was boiled with potash, the solution treated with an excess of hydrochloric acid, and the alumina then precipitated by carbonate of ammonia.

4. The insoluble residue (3) was dissolved in hydrochloric acid, and the iron precipitated by succinate of soda or ammonia with the usual precautions.

5. The lime was precipitated by oxalate of ammonia from the solu-

* Chem. Gaz., vol. iv. p. 296.

tion (2), after treatment with ammonia. The precipitate, which consisted of oxalate of lime mixed with oxalate of manganese, was incinerated at a bright red heat, and then digested with dilute acetic acid, which dissolved the lime and left the brown oxide of manganese. A slight excess of sulphuric acid was added to the solution of acetate of lime; the whole was evaporated to dryness, and heated to redness; from the sulphate of lime thus obtained the lime was calculated.

6. The solution (4), after separation of the iron, was added to solution (5) after separation of the lime. The manganese was precipitated by hydrosulphate of ammonia in a close vessel, and in every instance at least twelve hours were allowed for precipitation. The sulphuret of manganese was dissolved in hydrochloric acid, and precipitated by carbonate of potash. The carbonate of manganese was incinerated at a bright red heat for a considerable time. The oxide of manganese thus produced was estimated as $MnO + Mn^{o} O^{3}$.

7. The solution (6), after precipitation of the manganese, was digested with excess of hydrochloric acid until the sulphur eliminated by decomposition of the excess of hydrosulphate of ammonia had completely separated. The magnesia was precipitated by phosphate of soda and excess of ammonia. Generally twenty-four or forty hours were allowed for complete precipitation. The precipitate was washed with ammonia-water until no sensible residue was left by evaporation on a plate of glass, then dried, and incinerated as usual.

8. To determine the potash, the slag was digested as usual in hydrochloric acid, the iron peroxidized by nitric acid, and the solution then treated with excess of carbonate of ammonia. The filtrate was evaporated to dryness, and the ammoniacal salts were expelled by heat. The residue was treated with boiling water, and the solution filtered from the brownish residue. The filtrate was evaporated to dryness after the addition of excess of sulphuric acid. The residue was dissolved in water, acetate of baryta added in excess, the sulphate of baryta separated by filtration, and the filtrate was evaporated to dryness, and afterwards heated to redness. The solution contained the potash as carbonate; hydrochloric acid was added, and from the amount of chloride obtained by evaporation and heating to low redness, the potash was estimated. Berzelius's method of separating potash from magnesia by oxide of mercury was also occasionally resorted to.

9. The sulphur was determined either by oxidizing with strong nitrous acid, or by fusing with nitrate of potash and a mixture of carbonate of potash and soda. Chloride of barium was added to the acid solution. From the sulphate of baryta produced the sulphur was estimated.

The calculations have been made from the tables in the French translation of Rose's work by Peligot (Paris, 1843).

Nos. 1, 2, 3, 4 and 6 were obtained from hot-blast furnaces; No. 5 from a cold-blast furnace; Nos. 1, 2, 3 and 4, from the neighbourhood of Dudley; No. 5, from Tipton; and No. 6, from Belgium.

No. 1. Hardness = 6. Spec. grav., 2·9052 at 66° F. It yielded—

				Oxygen.
Silica	38·05			19·76
Alumina	14·11			6·59
Lime	35·70	10·03		
Magnesia	7·61	2·94		13·35
Protoxide of manganese	0·40	0·09		
Protoxide of iron	1·27	0·29		
Potash	1·85			0·31
Sulphuret of calcium	0·82			
Error of loss	0·19			
	100·00			

Phosphoric acid was not present.

No. 2. Hardness = 6. Spec. grav., 2·9152 at 66° F.

				Oxygen.
Silica	38·76			20·13
Alumina	14·48			6·76
Lime	35·68	10·02		
Magnesia	6·84	2·55		12·89
Protoxide of manganese	0·23	0·05		
Protoxide of iron	1·18	0·27		
Potash	1·11			0·19
Sulphuret of calcium	0·98			
Error of loss	0·74			
	100·00			

No. 3. Hardness = 6. Spec. grav. at 64° F., 2·9242.

				Oxygen.
Silica	37·63			19·55
Alumina	12·78			5·97
Lime	33·46	9·40		
Magnesia	6·64	2·48		13·46
Protoxide of manganese	2·64	0·67		
Protoxide of iron	3·91	0·91		
Potash	1·92			0·32
Sulphuret of calcium	0·68			
Error of loss	0·34			
	100·00			

No. 4. Hardness = 5·5. Spec. grav. at 64°, 2·9187.

				Oxygen.
Silica	37·91			19·69
Alumina	13·01			6·08
Lime	31·43	8·73		
Magnesia	7·24	2·81		12·27
Protoxide of manganese	2·79	0·52		
Protoxide of iron	0·93	0·21		
Potash	2·60			0·44
Sulphuret of calcium	3·65			
Error of loss	0·44			
	100·00			

Phosphoric cid was not present.

No. 5. Hardness = 5·7.

			Oxygen.
Silica	39·52		20·50
Alumina	15·11		7·06
Lime	32·52	9·60	
Magnesia	3·49	1·35	12·05
Protoxide of manganese	2·89	0·64	
Protoxide of iron	2·02	0·46	
Potash	1·06		0·17
Sulphuret of calcium	2·15		
Error of loss	1·24		
	100·00		

No phosphoric acid present.

No. 6:—

			Oxygen.
Silica	42·06		20·81
Alumina	12·93		6·05
Lime	32·53	9·14	
Magnesia	1·06	0·41	11·18
Protoxide of manganese	2·26	0·51	
Protoxide of iron	4·94	1·12	
Potash	2·69		0·46
Phosphoric acid 0·19 / Alumina 0·12	0·31*		
Sulphur 0·45 / Calcium 0·58	1·03		
Error of loss	0·19		
	100·00		

The phosphoric acid was determined thus:—The alumina and oxide of iron were fused for a considerable time with bisulphate of potash. The mass was digested with hydrochloric acid; some flocculent matter remained undissolved. To the solution tartaric acid was added, and afterwards chloride of magnesium and excess of ammonia. Two days afterwards minute crystalline particles were observed adhering to the glass. On examination with a simple microscope, the well-known star-shaped crystals of phosphate of magnesia and ammonia were immediately recognised. The solution was allowed to stand several days afterwards. The minute quantity of crystals was collected on a filter, and washed with cold ammonia-water, until no sensible residue was left by evaporation on a plate of glass. After incineration, the phosphate of magnesia weighed 0·06. The phosphoric acid is admitted to exist in combination with the alumina.

From an examination of the preceding analyses, it is evident that the following formula is the correct expression of the composition of this series:—

$$Al^2O^3,\ SiO^3 + 2\,(3(Ca,\ Mg,\ Mn,\ Fe)\,O,\ SiO^3).$$

* Estimated as $2Al^2O^3,\ 3PO^5$ $(51{\cdot}44\times2+55{\cdot}44\times3)$.

The formula differs from that of Vesuvian, in containing two equivalents of the silicate of lime series instead of one. Ivanov however has described a mineral from Slatoust, identical in composition with the preceding slags (Rammelsberg, Part 2. p. 258, and first supplement, p. 151); but Professor H. Rose informs us that the analysis of Ivanov has been clearly proved erroneous. Berthier has given the results of several analyses of slags from blast furnaces of nearly the same composition, but has incorrectly deduced the formula "(Ca, Mg, M, f)S+AS," which is that of Vesuvian. He has also omitted in his analysis of a slag from Dudley, protoxide of manganese, potash and sulphur, which were found in all the preceding analyses of slags from the same locality.

No. 7 was obtained from one of Mr. Dawes's hot-blast furnaces at Oldbury. It was found mixed with coke and other matters; it contains globules of iron, and sulphur may be readily observed deposited here and there upon the crystalline plates.

The crystals are thin square plates, the lateral faces of which are perpendicular to each other, and to the terminal faces. They appear to belong to the pyramidal system. They are white, and when very thin transparent.

Hardness = 5·7.

It contained sulphur in three states, free, combined as sulphuret, and also as sulphuric acid. The free sulphur was not estimated. Three analyses were made of it. They yielded:—

	a.	*b.*	*c.*	Mean.		Oxygen.
Silica	28·28	28·36		28·32		14·71
Alumina	24·22	24·27		24·24		11·33
Lime	40·39		39·96	40·12	11·27	12·42
Magnesia	2·94		2·62	2·79	1·08	
Protoxide of manganese	0·07			0·07	0·01	
Protoxide of iron	0·27			0·27	0·06	
Potash with trace of soda				0·64		0·11
Sulphate of lime				0·26		
Sulphuret of calcium				3·38		
				100·09		

This interesting specimen approximates very nearly in composition to Gehlenite, of which we introduce the following analyses for comparison (see Rammelsberg).

	Fuchs.	Oxygen.	Crystallized by V. Kobell.
Silica	29·64	15·38	31·0
Alumina	24·80	11·58	21·4
Lime	35·30	11·90	37·4
Magnesia	—		3·4
Proto-peroxide of iron	6·56	FeO	4·4
Water	3·30		2·0
	99·60		99·6

	Damour.		Oxygen.
Silica	31·60		16·18
Alumina	19·80	9·24	11·03
Sesquioxide of iron	5·97	1·79	
Lime	38·11	10·83	11·76
Magnesia	2·20	0·85	
Soda	0·33	0·08	
Water	1·53		
	99·54		

	Slag 7. *Percy.* Oxygen.	Native Gehlenite. *Fuchs.* Oxygen.	Native Gehlenite. *Damour.* Oxygen.
Silica	14·71	15·38	16·18
Alumina bases	11·33	11·58	11·03
Lime bases	12·42	11·90	11·76

In slag 7 we may probably be justified in regarding the sulphate of lime and sulphuret of calcium as impurities, and in no way connected with the formula; just as the water, which appears to exist in natural Gehlenite in variable proportion, may be similarly regarded. Metallic iron and fragments of coke being mixed up in the slag, the crystalline plates were carefully selected as free from impurity as possible.

The oxygen of the silica is to the oxygen in either the alumina or lime bases in the proportion of 4 to 3. This leads to the formula

$$3(3CaO,\ Si\,O^3)+3Al^2\,O^3,\ Si\,O^3,$$

or as represented by Berzelius's method of notation,

$$3\dot{C}a^3\,\ddot{S}i+\ddot{A}l^3\,\ddot{S}i,$$

which also appears to represent the constitution of Gehlenite more nearly than $2\dot{C}a^3\,\ddot{S}i+\ddot{A}l^2\,\ddot{S}i$, which is usually assigned to it.

We are unable to conjecture why the latter formula should have been preferred to the former, unless because the combination $\ddot{A}l^3$, $\ddot{S}i$ was supposed improbable; examples however of such a combination are afforded by Kollyrite $\ddot{A}l^3\,\ddot{S}i+15\dot{H}$, Heterokline $\ddot{M}n^3\ddot{S}i$, and Sismondine $4Fe^3\,\ddot{S}i+5\ddot{A}l^3\,\ddot{S}i+15\dot{H}$.

We may also call attention to the fact, that the slag in question has the same hardness as natural Gehlenite.

Admitting this slag to be really Gehlenite, the circumstance of its production at a high temperature in an iron furnace, may possibly be made available by the geologist in explaining the formation of the rocks in which the natural mineral occurs in Fassathal in the Tyrol. M. Krantz of Berlin informs us that it is found mixed with carbonate of lime between greenstone and felspar porphyry.

No. 8. This specimen was also presented to us by Mr. Dawes. It was obtained during the process of remelting cast iron with lime in a small cupola.

It forms a mass of pearl-gray slag containing imbedded long yellow crystals which appear to be square prisms with the angles truncated, cleavable perpendicular to the axis of the prism. In part of the specimen the crystals are very fine and radiated.

Nitrous acid was employed, instead of hydrochloric, to decompose this slag. It yielded—

			Oxygen.
Silica	45·59		23·68
Alumina	11·88		5·18
Lime	38·20	10·73	
Protoxide of manganese	0·91	0·20	11·18
Protoxide of iron	1·11	0·25	
Sulphuret of calcium	1·76		
Error of loss	0·55		
	100·00		

Without attempting to extort from the preceding analytical results a precise atomic expression, we may state that probably the formula of Humboldtilite ($3\dot{R}^2\,\dddot{S}i + \dot{\underline{R}}\,\dddot{S}i$), as deduced from the analysis of Von Kobell, nearly represents the constitution of this slag.

Damour assigns a different formula for Humboldtilite, which he believes to be identical with Mellilite; and this formula is precisely that which we have given for the first series of blast-furnace slags.

Nos. 9 and 10. The two following specimens were communicated by M. Krantz, the well-known mineralogist of Berlin. They were labelled, Olsberger Furnaces, on the Rhine.

No. 9 contains a drusy cavity with projecting crystals, which are not sufficiently bright for measurement with the reflective goniometer. They appear to belong to the oblique prismatic system. They have a single end face which is not at right angles to the axis of the prism. Hardness = 5. No. 10 is a mass exhibiting a radiated crystalline structure, the individuals of which are too small for measurement. Hardness = 5·7.

On one side of each of these specimens are attached minute scales of graphite.

The three following slags not being decomposable by hydrochloric acid, the method of fusion with a mixture of equal parts of carbonate of potash and soda was resorted to.

No. 9 yielded—

	a.	*b.*	Mean.	Oxygen.
Silica	53·27	53·48	53·37	27·72
Alumina	5·06	5·19	5·12	2·81
Lime	30·65	30·78	30·71	8·62
Magnesia	9·47	9·54	9·50	3·67
Protoxide of manganese	1·41	..	1·41	0·31
Protoxide of iron	1·02	0·89	0·95	0·21
			101·06	

No. 10:—

			Oxygen.
Silica	53·76	.....	27·93
Alumina	4·76	.....	2·22
Lime	29·48	.....	8·28
Magnesia	9·82	.....	3·80
Protoxide of manganese	1·30	.....	0·29
Protoxide of iron	1·48	.....	0·34
	100·60		

With the exception of a few small crystals in a drusy cavity in No. 9, the crystallization of the two preceding slags is confused, so that we could scarcely hope to deduce from their composition a satisfactory formula. The oxygen of the acid being nearly double that of the bases, the slag is formed of bisilicates, and evidently approximates very nearly in composition to some varieties of augite (pyroxene) containing alumina. Several analyses of augite giving about the same per-centage of alumina may be found in the first part of Rammelsberg's admirable work previously referred to. The silicate of alumina exists probably as an accidental constituent, and does not enter into the formula (Vide 'Handbuch der Chemie,' von L. Gmelin, vol. ii. p. 383).

No. 11. This slag, which is brown, porous, and confusedly crystalline, was brought by Mr. Blackwell from the hot-blast furnaces called L'Espérance, at Seraing, near Liège, in Belgium. It yielded, when fused with the carbonate of potash-soda mixture—

			Oxygen.
Silica	55·77	.....	28·97
Alumina	13·90	.....	6·49
Lime	22·22	6·24	8·09
Magnesia	2·10	0·81	
Protoxide of manganese	2·52	0·56	
Protoxide of iron	2·12	0·48	
Potash	1·78	.....	0·30
	100·41		

As the crystallization was very confused, and as the analytical results do not point satisfactorily to a formula, we do not attempt to deduce any rational expression of the composition of this slag.

No. 12. This specimen of "Refinery Cinder" was produced in the Bromford Iron Works, near Birmingham, and was communicated by Mr. John Dawes. The process of refining, which is not now extensively practised in Staffordshire, consists in exposing the surface of melted cast iron to the action of a blast. The products are refined or white iron, and "refinery cinder" or slag.

No. 12, fused with the carbonate of potass-soda mixture and nitrate of potash*, gave

* I have no doubt that phosphoric acid and sesquioxide of iron existed in this slag in small quantity.

			Oxygen.
Silica	22·76	.....	11·83
Protoxide of iron	61·28	.....	13·95
Protoxide of manganese	3·58	.....	0·70
Alumina	7·30	.....	3·41
Lime	3·41	.....	0·97
Magnesia	0·76	.....	0·29
Sulphur	0·46		
Error of loss	0·45		

From the identity in crystalline form of this slag with the one succeeding, we are inclined to regard it as a mixture of silicate of protoxide of iron with a considerable amount of impurity, represented especially by the alumina. This view would also appear to receive confirmation from an inspection of the slag itself. We need scarcely refer to the numerous instances of well-formed crystals containing much foreign matter, so that there seems to be nothing improbable in this view respecting the composition of the crystals of this slag, which are certainly not perfectly formed.

No. 13. The following beautifully crystallized specimen was presented by Mr. Dawes. It was found in the flue of a puddling furnace, where it had probably been exposed to a high temperature for a considerable time.

The surface of this slag is covered with bright black crystals, exhibiting occasionally an iridescent tarnish. The crystals belong to the prismatic system.

Hardness = 6. Specific gravity at 65° F., 4·0805.

It was found to contain silica, protoxide and sesquioxide of iron, protoxide of manganese, alumina, lime, magnesia, sulphur as sulphuret, and phosphoric acid. It was decomposed by long digestion with dilute hydrochloric acid. The silica, however, obtained by this means was more or less gray; and in order to obtain it perfectly white, it was fused with the carbonate of potash-soda mixture, and the fused mass, which had a bluish-green colour, was decomposed with hydrochloric acid. The solution was treated with nitric acid to peroxidize the iron; ammonia was then added in slight excess, and the analysis continued in the manner formerly described. The proportion of the two oxides of iron, the phosphoric acid and the sulphur, were determined by separate analyses.

The protoxide and peroxide of iron were determined by the gold process.

			Oxygen.
Silica	29·60	.....	15·37
Protoxide of iron	48·43	.....	11·02
Sesquioxide of iron	17·11	.....	5·24
Protoxide of manganese*	1·13	.....	0·25
Alumina	1·28	.....	0·59
Lime	0·47	.....	0·13
Magnesia	0·35	.....	0·13
Phosphoric acid	1·34	.....	0·75
Sulphuret of iron	1·61		
	101·32		

* Probably a portion existed as a superior oxide.

These crystals closely resemble olivine in their form and chemical constitution, the magnesia being replaced by protoxide of iron.

Crystals similar to these in form, composition and mode of occurrence, have been described by Mitscherlich in the Annales de Chimie, vol. xxiv. Measurements of crystals of the same form, and a comparison of their angles with those of olivine, may be found in the third volume of the Transactions of the Cambridge Philosophical Society.

Estimating the whole of the iron as protoxide, the composition would be nearly that of $\dot{Fe}^3\dddot{Si}$, the formula assigned by Thomson to the mineral from Ireland, named "Anhydrous silicate of iron." Now, this slag had evidently been in a position favourable to the absorption of oxygen, namely, the flue of a puddling furnace; and we shall probably be justified in supposing that, after crystallization as silicate of protoxide of iron, oxygen may have been absorbed, and that the crystal may consequently be regarded to a certain extent pseudomorphous. In the case of the following slag, which is similar to the one in question, it was found by experiment that the powder of the slag readily absorbed oxygen by calcination in the air. If this view be admitted, the slag will in constitution as well as form resemble olivine, the magnesia of the latter being replaced by protoxide of iron.

No. 14. This slag was found by Mr. Twamley at the Bloomfield iron-works, Tipton, in a heap of calcined puddling furnace slag, technically called "tap cinder." The proprietors of these works have secured by patent the application of calcined tap cinder for the beds of puddling furnaces. It is stated that, by the process of calcination, which is conducted in large kilns similar to brickkilns during a fortnight or three weeks, the slag is rendered much less fusible, and is therefore well-adapted to the purpose to which it is applied. The analysis will probably explain this fact. The heat of the kilns appears to be sufficient to soften and agglutinate the pieces of slag together, but not to effect perfect fusion.

This slag is a mass of large iron-gray crystals, the faces of which though even are much too dull to be measured with the reflective goniometer. The general resemblance of their forms, however, to those of No. 12 is so close as to leave no doubt of their crystalline identity.

Specific gravity = 4·1885 at 64°·5 F.

It attracts the magnetic needle strongly. It yielded on analysis—

			Oxygen.
Silica	23·86	.....	12·41
Protoxide of iron	39·83	.....	9·07
Sesquioxide of iron	23·75	.....	7·28
Protoxide of manganese	6·17	.....	1·38
Alumina	0·91	.....	0·42
Lime	0·28	.....	0·08
Magnesia	0·24	.....	0·09
Phosphoric acid	6·42	.....	3·60
Sulphuret of iron	0·62		
	102·08		

We regard this slag as similar in constitution to the preceding, the alumina, some of the sesquioxide of iron, and the phosphoric acid being present as impurities. The presence of so large a quantity of sesquioxide of iron in this slag is probably to be explained by its long exposure in the kiln, during which it was in a condition favourable to the absorption of oxygen. The powder of the slag, when heated to redness in a platinum crucible, changes colour, acquiring a brown tint, and increasing in weight. The quantity of phosphoric acid is also remarkable, and is well-deserving of the attention of those engaged in the smelting of iron. Berthier has given the analysis of a refinery slag from Dudley (Traité des Essais, t. 2. p. 289), containing 7·2 per cent. of phosphoric acid. It is found that when puddling furnace slag (tap cinder) is worked with the ordinary ores of iron, such as argillaceous ore and hæmatite, the iron is liable to be "cold short," or possess that property which is known to be dependent upon the presence of phosphuret of iron. Now it is evident that in smelting tap cinder, which will probably always be found to contain a sensible amount of phosphoric acid, the manufacturer will be introducing into the furnace the very element, in a concentrated form, which it is one object of the puddling furnace to remove, namely, phosphorus. An immense quantity of iron slag, far richer than many iron ores, is annually thrown away, and it may be that the presence of phosphorus in sensible quantity is one of the causes which prevents the resmelting of this slag with advantage. This fact has not yet sufficiently attracted the attention of those engaged in the manufacture of iron. The discovery of a method of extracting economically good iron from these rich slags would be of great advantage to the country, and could not fail amply to reward its author.

We have remaining an extensive series of slags from various metallurgical works, which we have not yet had time to investigate, but we hope to be able to continue our labours in this department, and to present to the Association a second report at no distant period. Amongst them are several specimens of beautifully crystallized octahedral or magnetic oxide of iron, and many other crystals from the copper furnaces.

On Proteine. *By* Prof. MULDER.

[Extracted from a Letter written by Mulder to Dr. Fresenius, by whom it was communicated to Prof. Erdmann, dated March 21, 1847.]

As you are aware, my last investigations were made upon proteine. I freely and candidly confess, that the quantity of sulphur contained in it is greater than I had supposed; but I am much astonished that nothing has been said regarding its condition. All the observations have been confined to *that* portion of the sulphur which, under the influence of an alkali, blackens acetate of lead; but it also contains some which does not do this.

In fact, all proteine contains a *variable* quantity of hyposulphurous acid, the proteine from fibrine for instance 1 per cent., which quan-

tity may be *increased* or *diminished*; it is very easy to prove that it is really hyposulphurous acid, produced by the action of the alkali upon the albumen, &c.; the sulphur and phosphorus exist in albumen, horny matter and fibrine as amides, as S, NH^2 and P, NH^2. When 2(S, NH^2) act upon 2HO, S^2O^2 is formed, a part of which combines with the proteine, and $2NH^3$, which is evolved. As the sulphur becomes separated, ammonia is evolved. By means of the ordinary method used for obtaining hyposulphurous acid, I have procured compounds of S^2O^2 with proteine, in which exactly the same quantities of sulphur exist as in albumen, fibrine, &c., in which case $\frac{1}{2}S^2O^2$ replaces 1 equiv. S, NH^2.

Fleitmann's determinations of the nitrogen are too high. Proteine, which contains 1·4 per cent. of sulphur, as S^2O^2, yields only 14·4 per cent. of nitrogen. It is impossible, by the qualitative method, as it is called, of determining the nitrogen, to determine the nitrogen in substances in which the carbon burns with such difficulty.

If we now seek for the composition of the proteine in the old analyses (C = 75·12), we have—

	Proteine from albumen.	Reduced by the deduction of the S and O combined with it to form S^2O^2.	
Carbon.....	53·7	53·7	54·9
Hydrogen....	6·9	6·9	7·0
Nitrogen	14·4	14·4	14·7
Oxygen	23·6	22·9	23·4
Sulphur	1·4*		
	100·0	97·9	100·0
	Albumen†.	Reduced as above for S, NH^2.	
Carbon.....	53·6	53·6	55·1
Hydrogen....	7·0	6·9	7·0
Nitrogen	15·7	14·5	14·9
Oxygen	22·3	22·3	23·0
Sulphur	1·4		
	100·0	97·3	100·0
	Cow's hoof.	Reduced for S, NH^2.	
Carbon.....	50·2	50·2	55·2
Hydrogen....	6·8	6·3	6·9
Nitrogen	17·3	13·3	14·7
Oxygen	21·1	21·1	23·2
Sulphur	4·6		
	100·0	90·9	100·0

I have selected these examples to show that the *substance free from sulphur* is the same when its combinations are reduced by S^2O^2 or S, NH^2.

* According to Fleitmann.

† I have omitted the small amount of phosphorus.

Fibrine really yields more oxygen, and the same substance occurs in legumine and cow's horn.

	Fibrine.	Reduced for S, NH^2.	
Carbon.....	52·7	52·7	53·8
Hydrogen....	6·9	6·8	6·9
Nitrogen	15·5	14·6	14·9
Oxygen	23·9	23·9	24·4
Sulphur	1·0		
	100·0	98·0	100·0
	Horn.	Reduced for S, NH^2.	
Carbon.....	50·1	50·1	53·8
Hydrogen....	6·8	6·3	6·8
Nitrogen	16·2	13·2	14·2
Oxygen	23·5	23·5	25·2
Sulphur	3·4		
	100·0	93·1	100·0
	Legumine from green peas (according to Norton's analyses).	Reduced for S, NH^2 and P, NH^2.	
Carbon.....	50·8	50·8	53·6
Hydrogen....	6·6	6·3	6·8
Nitrogen	15·6	13·9	14·7
Oxygen	23·8	23·8	25·0
Sulphur	0·8		
Phosphorus ..	2·4		
	100·0	94·8	100·0

At present I refrain from furnishing you with any more extended formulæ; but I think that our real knowledge of the substance under consideration now commences to progress.—*Journ. für Prakt. Chem.*, 1847, No. 5.

On the Presence of Silica in the Feathers of Birds. *By* Dr. G. Besanez.

In a comparative examination of birds' feathers, the author found silica constantly present, it being probably of the same importance to the beards of feathers as phosphate of lime to the bones. The silica was determined by treating the ash with hydrochloric acid, evaporating to dryness, again exhausting the residue with hydrochloric acid, separating the silica by filtration, then washing and heating it to redness.

	Ash.	Silica.
White goose feathers (beard) gave	3·83	1·47 p. c.
... ... (quill) gave.....	0·54	0·09 ...
... ... (pith) gave.....	0·57	
Black magpie feathers (beard).....	3·78	1·51 ...
Green and blue parrots' feathers (beard)..	5·31	1·19 ...
Black storks' feathers (beard)	3·04	0·94 ...

V. Laer having pronounced the hair to contain silica, the author examined the spines of the hedgehog. They yielded 1·11 per cent. of ash and 0·18 per cent. of silica. Hence horn, as also the quill and pith of feathers, contain less inorganic matter and silica than the beard of feathers. All the ashes contained iron, especially those of the parrots' feathers; they also contained phosphate of lime, basic phosphate of soda, but no sulphates nor chlorides. The amount of silica present averaged 32·96 per cent. of the ashes, which is undoubtedly more than can be considered as accidental. The smallest quantity of silica was found in the feathers of the insectivorous stork, the largest in the granivorous birds.—*Ann. der Chem. und Ph.*, lxi. p. 46.

On the Presence of Alumina in Plants.
By Prince Salm-Horstmar.

Much doubt has lately been thrown on the presence of alumina in plants. Berzelius, however, asserts that it is present in *Lycopodium complanatum* and *Helleborus niger*. This induced the author to investigate its occurrence in these and some other plants.

Some *Lycopodium complanatum*, which had been collected in February, was boiled with distilled water for half an hour, the filtrate evaporated in a platinum dish, the yellow gummy residue incinerated, the ash dissolved in muriatic acid, evaporated to dryness, again dissolved in muriatic acid, filtered, the filtrate treated with muriate of ammonia, then with pure ammonia, the precipitate dissolved in a small quantity of muriatic acid, digested with solution of potash in excess in the platinum dish, and filtered. The filtrate yielded a precipitate of alumina and phosphate of alumina on the addition of muriate of ammonia.

0·35 grm. of the ash of the green parts of this Lycopodium were treated with muriatic acid, no effervescence occurred; the solution was evaporated to dryness in the platinum capsule, and the mass well moistened with muriatic acid; after standing some time, it was dissolved in water, filtered, the filtrate treated first with muriate of ammonia, then pure ammonia, the precipitate washed, removed from the filter while moist and dissolved in muriatic acid, treated with excess of caustic potash in a platinum capsule, digested with heat, when the greater part dissolved, it was filtered, the filtrate treated with silicate of potash, and heated to ebullition in a glass vessel, the washed precipitate dissolved while moist in muriatic acid, evaporated to dryness in platinum until the odour of chlorine had disappeared, thoroughly moistened with muriatic acid, treated with water, the silica separated by filtration, and the filtrate precipitated with carbonate of ammonia; the precipitate, when well-washed and heated to redness, weighed 0·135 grm., and consisted of alumina; hence the ash contains 38·5 per cent. of alumina. It acquired a beautiful blue colour when treated before the blowpipe with a solution of nitrate of cobalt.

This ash contained, moreover, 16 per cent. of silica soluble in

potash, and only 6 per cent. of lime. The other constituents were magnesia, potash, soda, manganese, iron, phosphoric acid and sulphuric acid, which were not accurately determined. The aqueous solution was not alkaline in reaction. This lycopodium grew upon a yellow, aluminous, sandy heath, which contained only a trace of humus.

0·35 grm. of the ash of *Juniperus communis*, which was growing close to the lycopodium, was tested for silica. The ash was prepared from the summits of the shoots, which were thickly covered with needles. Alumina was decidedly present, but the quantity did not amount to a millegramme. It contained only 2·5 per cent. of silica, but 28·5 per cent. of lime.

Moreover, in 0·5 grm. of the ash of *Erica vulgaris*, which also grew close to the *Lycopodium complanatum*, a small but appreciable quantity of alumina was present with 17 per cent. of silica soluble in solution of potash. The delicate summits of the shoots covered with leaves were the only parts used for this examination.

Alumina was also found in the leaves of *Helleborus niger*, which had grown in a garden soil abounding in humus.

The leaves of *Pinus sylvestris* contained no trace of alumina. The tree grew upon a rich sandy soil.

Hence there is no doubt that certain plants contain alumina.

The remarkable circumstance, that the ash of *Lycopodium complanatum* contains more than 38 per cent. of alumina, *Juniperus communis*, growing close to it, a mere trace, whilst many plants, according to recent analyses, contain none, appears to justify the conclusion that the roots of plants containing alumina either exert a peculiar catalytic power upon the aluminous compounds with which they are in contact, or excrete an acid; for were the aluminous constituents of the soil soluble *per se* in the fluids of the soil, they would also be absorbed by other plants.

This consideration induced the author to test the reaction of the roots of *Lycopodium* and *Juniperus*; and he found that the perfectly fresh uninjured smaller roots of *Lycopodium complanatum*, free from the soil, when placed upon moistened litmus-paper, had an acid reaction, whilst the root of *Juniperus communis* did not exert this action.—*Journ. für prakt. Chem.* April, 1847.

On the Nature and Chemical Constitution of the Emulsine contained in Almonds. *By* F. Ortloff.

The emulsine was prepared for examination in the following manner:—1 lb. of sweet almond paste, as free as possible from oil, was stirred up with about 3 times the weight of distilled water in a broad glass cylinder or in a wide-necked flask, so that after standing for some time the liquid is clear for a space of from 1 to 2 fingers' breadth above the paste; the whole is then left at 66° to 77° F. until fermentation has set in, and a thick membranous stratum has formed on the surface of the almond-paste. After 5 or 7 days at the furthest, the entire mass is strained and filtered as quickly as

possible. The acid slightly-opalescent liquid, which has a peculiar odour, is now mixed with about an equal weight of alcohol of 0·803 spec. grav. until a filtered sample is no longer precipitated by alcohol. The precipitate is collected on a filter, washed with some spirit, and dried at a temperature below 100° F. In order to remove the magnesia salts which it still contains, the dried emulsine is placed in water for 24 hours, being frequently shaken. The filtered solution, which still contains traces of lime which are very difficult to remove, is now suited for experiment. A further quantity of emulsine can be extracted from the residue of the first straining by allowing it to stand for 24 hours with water. Robiquet treated the solution of emulsine with acetate of lead and sulphuretted hydrogen; but emulsine is likewise precipitated by the lead salt; so that when a sufficient quantity of lead salt is added, no emulsine is contained in the solution. The above solution immediately yields, when mixed with amygdaline, a distinct odour of prussic acid and oil of bitter almonds, and a precipitate of prussian blue is formed with protosulphate of iron, caustic potash and muriatic acid. When dry, emulsine forms a slightly reddish-gray gummy mass, which readily breaks in sharp-edged pieces; the cleavage is smooth or slightly conchoidal, somewhat horny, transparent, and externally with a vitreous or fatty lustre. It is tasteless, and has a peculiar sweetish odour; the powder is white or faintly reddish; when heated on platinum, it puffs up, and burns with the odour of burning horn, leaving a residue of phosphate of lime. It is decomposed by heating it with sulphuric acid, becoming black, and giving off a gas, but without the odour of sulphurous acid. Heated with dry potash, it gives off a large quantity of ammonia, less with a solution of potash and barytic water. It is insoluble in alcohol and æther, and very sparingly oluble in spirit; the aqueous, tolerably-concentrated solution is faintly opalescent and somewhat acid; when heated, it becomes turbid far below the boiling-point and coagulated, whereby it loses its property of acting upon amygdaline. The coagulated emulsine dissolves readily in acids. Mineral and vegetable acids prevent the coagulation on boiling; and if under these circumstances a precipitate is formed, it always consists of albumen, the mixture not having stood sufficiently long to allow the whole of the albumen to deposit. However, when the emulsine still contains albumen, the latter is completely deposited by setting the solution of emulsine aside for a couple of days. The solution of emulsine becomes gradually turbid, and of a somewhat disagreeable odour after standing for several weeks, but not putrid, and still acts upon amygdaline; but after 4 to 6 weeks all action has disappeared.

Emulsine yields white precipitates with perchloride of iron, gold and platinum, which are easily soluble in an excess and in acids; also with the chlorides of barium and calcium, but not with the chlorides of magnesium, potassium and sodium; perchloride of mercury produces an abundant flocculent precipitate, insoluble in an excess, but easily soluble in nitric acid, as do likewise protochloride of tin, barytic and lime water, proto- and pernitrate of mercury, and

acetate of lead. The precipitates with carbonated alkalies, sulphate of copper and zinc, and with alum, are soluble in an excess. Tannic acid gives a precipitate insoluble in an excess and difficult of solution in nitric acid; ferrocyanide of potassium produces no precipitate. The author could not observe the rosy colour produced by tincture of iodine, as stated by Robiquet. The above properties sufficiently distinguish emulsine from albumen. Dried at 212°, it afforded, after deducting 17·55 per cent. ash—

Carbon	27·498	27·665	28·332	27·998
Hydrogen.....	5·043	5·380	5·716	5·581
Nitrogen	9·620	8·850	9·350	

which corresponds, according to the author, to the formula $C^{10} H^{12\frac{1}{2}} NO^{16}$, or, according to Ludwig, $2C^7 H^8 NO^{11}$. This formula, however, is as yet of little value, as it was found impossible to obtain constant combinations with emulsine. The emulsine analysed by Thompson and Richardson, and likewise by Dumas, certainly contained albumen.

According to the author, emulsine contains *no* sulphur, as it yields no sulphuretted hydrogen on spontaneous decomposition, and no sulphuret of potassium when boiled with solution of potash; nor can it be regarded as a proteine compound, since it dissolves in concentrated hydrochloric acid to a perfectly colourless solution. The reaction of emulsine upon amygdaline depends upon the quantity in solution of the former, and only so much oil of bitter almonds is formed as can dissolve in the liquid. If the liquid is warmed, but so as not to coagulate the emulsine, a portion of the oil is volatilized and more is formed immediately; but if the heat is raised until the liquid boils, the emulsine is coagulated, and all further formation of oil of bitter almonds ceases.

When amygdaline is added to a solution of emulsine, the former is, as is well-known, entirely decomposed. On a further addition of amygdaline, the same process is repeated, until finally, according to Liebig, a period occurs when the decomposition ceases, and a sugary liquid is obtained. According to the author, this is owing to the amount of water, and a decomposition again commences when more water is added. The tenacious inspissated syrup, to which 10 times the quantity of amygdaline was added, on solution in water and mixing with amygdaline, immediately yielded a strong odour of prussic acid and bitter almonds. According to Thompson and Richardson, emulsic acid is formed on boiling emulsine with barytic water, with disengagement of ammonia; according to the author, the emulsine is coagulated in flakes, and the formation of emulsic acid is still very problematical.—*Archiv der Pharm.*, xlvii. p. 12.

On the Action of Potash upon Pyroxyline (Gun-Cotton). *By* Dr. Van Kerckhoff.

When well-washed pyroxyline is placed whilst still moist in contact with caustic potash, slow solution occurs even at ordinary temperatures; this proceeds with much more rapidity at about 140° F.

From the experiments detailed below, it appears that this difference of temperature exerts a different effect; for when the temperature was kept low, tolerably considerable excess of potash being present, the substance precipitated by acetate of lead from the solution was different from that which was obtained when the solution which contained less excess of potash was exposed to a greater heat.

On examining this solution, I ascertained the interesting fact, that at one time citric acid or a body isomeric with it, at another tartaric acid was formed, whilst a considerable quantity of nitrite of potash and a comparatively small quantity of carbonate of potash existed in the fluid; for when the potash solution was slightly supersaturated with acetic acid, a copious amount of nitric oxide was formed, which was also evolved, but more copiously and with effervescence, on the addition of sulphuric acid. The fluid, when rendered as slightly acid as possible by acetic acid, yielded the characteristic colour on the addition of protosulphate of iron. In the potash solution, which had been treated with acetic acid (and which on the addition of pure potash was not rendered turbid), acetate of lead produced a slightly yellowish precipitate; and in the liquid filtered from this, basic acetate of lead produced another precipitate.

In another preparation, in making which the temperature rose somewhat higher, I also obtained a precipitate with acetate of lead, which was washed and decomposed by sulphuretted hydrogen; the solution thus obtained, when freed from the excess of sulphuretted hydrogen and filtered, was strongly acid, and reacted as follows:—When treated with chloride of iron or protochloride of manganese, no precipitate was produced on adding excess of ammonia even after some time. The solution, when neutralized with potash, yielded a white precipitate with chloride of calcium, which dissolved in cold potash, forming a clear liquid, which was rendered very turbid when boiled. Excess of lime-water produced a precipitate, which was quickly redissolved by muriate of ammonia. No precipitate was produced by solution of sulphate of lime. The evaporated fluid left a residue, which when heated gave the well-known odour of tartaric acid. The quantity of fluid obtained was so small, that I endeavoured in vain to make it crystallize; it was therefore evaporated in a water-bath; when it first dried to a syrup, and then, without the evolution of empyreumatic vapours, swelled into a porous yellowish-brown mass, which was readily soluble in water and alcohol.

When dried at 212°, this substance yielded on analysis with oxide of copper—

	Found.		
Carbon	33·86	8 =	34·04
Hydrogen	3·56	5	3·55
Oxygen	62·56	11	62·41
	100·00		100·00

This composition agrees accurately with that of the *tartrelic acid* discovered by Fremy; but since, according to his statement, it requires a much higher temperature to produce the latter, it remains

at present uncertain whether the acid I obtained is not an isomeric modification of it; the reactions however do not give support to this supposition.

The precipitate caused by basic acetate of lead in the acidified potash solution, dried at 220° F., was burnt; the lead was determined by Berzelius's method in a porcelain crucible. It yielded—

	Found.		
Carbon	7·37	12 =	7·36
Hydrogen	0·66	6	0·61
Oxygen	12·32	15	12·26
Oxide of lead	79·65	7	79·77
	100·00		100·00

The calculated composition also agrees accurately with that of a lead salt, consisting of 2 equivs. of basic and 1 equiv. of neutral tartrelate of lead—

$$2(3PbO, C^4 H^2 O^5) + PbO, C^4 H^2 O^5.$$

I once obtained a precipitate from the slightly acidified potash solution by acetate of lead, which when dried at 220° F. yielded—

	Found.		
	I.	II.	
Carbon.....	14·11	14·06	14·15
Hydrogen	1·15	1·21	1·18
Oxygen	18·88	18·87	18·87
Oxide of lead	65·86	65·86	65·80
	100·00	100·00	100·00

This result leads to the formula of the neutral citrate of lead.

I shall hereafter again prepare this salt, to separate the acid and to subject it to an accurate examination. There was no nitrogen in any of the compounds analysed. The formation of the last acid (whether it be really citric acid or a substance isomeric with it) is very easily explained from the composition of pyroxyline given by M. Reuter and myself: thus—

	C.	H.	N.	O.
1 equiv. pyroxyline	24	13	6	43
minus 6 equivs. nitrous acid			6	18
and 1 water		1		1
leaves 6 equivs. citric acid	24	12		24

As regards the formation of the tartrelic acid, this must be derived from further oxidation; which indeed readily occurs when nitrite of potash and free acetic acid are present, and may perhaps lead to a nearer insight into the relation of the two organic acids.—*Journ. für Prakt. Chem.*, 1847, No. 5.

The Action of Sugar upon the Teeth. *By* Prof. Marchand.

In several medical periodicals, and among others in Heller's 'Archiv,' i. p. 64, a notice is circulated, which emanates from Larrey

(taken by Heller from the 'Gazetta Medica di Milano,' 1844, No. 10), which states that the destructive action exerted by sugar upon the teeth is produced by the combination of the sugar with the lime of the teeth, hence the removal of the latter; and thus that teeth which are macerated in a saturated solution of sugar become opake and ultimately gelatinous. The enamel resists longer, inasmuch as, containing fluoride of calcium, it is less soluble than the sulphate of lime.

If these statements, which are absurdly copied, are based upon experiments, the latter must have been performed in a very remarkable manner. Solution of sugar in water certainly dissolves caustic lime more readily than pure water; but, as is well known, this is not the case with the carbonate and sulphate of lime and the fluoride of calcium; and M. Larrey will not probably be inclined to admit the existence of caustic lime in the teeth! Teeth and bones, which had remained in sugar and water for fourteen days, were not found softened; and the fluids exhibited the same traces of lime salts as are found when they are treated with pure water.—Erdmann and Marchand's *Journal*, 1847, No. 6.

Analysis of a Stone from the Urinary Bladder of a Pig. *By* Dr. L. Bley *and* E. Diesel.

This stone was of the size and shape of a small hen's egg, externally grayish-white and smooth, but rough in certain spots. It weighed 670 grs. When sawn through, it exhibited five layers, which were coloured more or less brown or white. The nucleus was very white, and internally of a bright ochre colour. The calculus was treated successively with water, alcohol, æther, nitric and muriatic acids. The latter caused the evolution of a little sulphuretted hydrogen, which must have arisen from the presence of sulphuret of lime. It yielded on analysis—

	Grains.
Albumen	4·500
Red resin	3·500
Green resin	0·500
Fat	1·500
Carbonate of lime	44·500
Ammonio-phosphate of magnesia	60·550
Sulphuret of calcium	2·236
Humic acid Silica	1·500
Water and loss	26·214
	145·000

Archiv der Pharm., 2 R. xlviii. p. 283–7.

ANALYTICAL CHEMISTRY.

On the Separation of Tin from Antimony. *By* Prof. H. Rose.

As is well known, the separation of these two metals is accompanied with many difficulties. The older method of Chaudet* recommends the use of hydrochloric acid for this purpose; but this is attended with success only when the action of the acid upon the antimony is weakened by the presence of a very large quantity of protochloride of tin. By this method, as also by that subsequently proposed by Gay-Lussac†, of precipitating the antimony from the solution of the two metals by means of metallic tin, the antimony alone is determined directly, and the amount of tin ascertained from the loss. Levol‡ has, on this account, modified the process suggested by Chaudet; he dissolves the alloy of the two metals in hydrochloric acid to which chlorate of potash has been added, precipitates both the metals from the solution by metallic zinc, and without decanting the solution of chloride of zinc, redissolves, by the addition of highly-concentrated hydrochloric acid, the tin, which is then precipitated by sulphuretted hydrogen; while the antimony is left behind undissolved.

This method has not been found to be accurate by Elsner§, as some antimony is dissolved with the tin by the acid; to which Levol has replied, that the presence of the chloride of zinc considerably weakens the action of the hydrochloric acid upon the antimony.

Whichever method is employed, the separation of these two metals is never so perfect as with other substances which do not behave in so analogous a manner towards reagents as tin and antimony. The method which I employ, but which to give satisfactory results must be carried out with great care, is as follows:—

Strong nitric acid is cautiously poured upon the metals, and when the violent oxidation has ceased, the whole is evaporated at a gentle heat, and the dry powder of the oxides fused in a silver crucible over an Argand lamp with an excess of hydrate of soda. The fused mass is softened with a large quantity of water, gently warmed, and the antimoniate of soda allowed to subside. When perfectly cold, the clear solution is passed through a filter; if this is done while it is still warm, the solution will contain some antimoniate of soda. The insoluble salt is again treated once or twice with water, allowed to settle and cool, and the liquid when perfectly clear passed through the filter. When the whole of the stannate of soda has been dissolved in this manner, the liquid which has been warmed with the antimoniate of soda remains opalescent; it must not be poured upon the filter, as it would pass through turbid. A small quantity of a dilute solution of carbonate of soda may be added to it, which renders it clear; but the edulcoration must not be continued for any length of time, as otherwise some antimoniate would be dissolved.

The moist antimoniate of soda is now treated in a beaker with a

* Ann. de Chim. et de Phys., iii. p. 376. † Ibid. xlvi. p. 222.
‡ Chem. Gaz., vol. iii. p. 62. § Chem. Gaz. vol. iv. p. 105.

mixture of hydrochloric and tartaric acids, in which it readily dissolves; and the filter, upon which but mere traces of the salt should have collected, washed with the same mixture. The antimony is then precipitated from the solution by sulphuretted hydrogen, and the amount of antimony estimated from the quantity of sulphuret obtained. I am at present accustomed to reduce the sulphuret of antimony by hydrogen in a porcelain crucible, through the lid of which a thin porcelain tube passes. This apparatus is now manufactured at the Royal Porcelain Works of Berlin. A gentle heat is carefully applied until the crucible no longer decreases in weight. After the reduction the inner side of the lid is coated with metallic antimony, which might lead to the belief that the result of the experiments must be inaccurate, which however is not the case.

The solution of the stannate of soda is acidified with hydrochloric acid. It is not requisite to add so much acid that the whole of the eliminated oxide of tin is again redissolved. It is merely necessary that the solution should strongly redden blue litmus-paper. Upon this, sulphuretted hydrogen is passed into it. The sulphuret of tin is converted by roasting into oxide. When it has been dried, it frequently decrepitates, which by want of care may occasion a very considerable loss. It is on this account preferable to place it with the filter, while still moist, in a porcelain crucible, and to heat it for a long time very gently and with access of air, to expel the sulphur at the lowest possible temperature. If a strong heat be given at the commencement, white fumes of oxide escape, especially when the air has free access. The higher sulphuret of tin has the property of subliming somewhat at certain temperatures; the vapours are oxidized by contact with the air, and form oxide of tin. This is also the cause of a white sediment of oxide of tin being formed upon charcoal when sulphuret of tin is heated on charcoal before the blowpipe. A strong heat should not be applied until there is no longer any perceptible odour of sulphurous acid. After being strongly ignited, a piece of carbonate of ammonia is placed in the crucible; and after its volatilization, a strong heat applied with access of air, in order to expel the whole of the sulphuric acid formed. A small decrease in weight will be perceived.

The oxide of tin thus obtained never appears perfectly white; and the sulphuret of tin precipitated by sulphuretted hydrogen does not possess a purely yellow colour, which appears to arise from melting the metallic oxides with hydrate of soda in the silver crucible, traces of oxide of silver being removed by the alkaline solution.

The results do not attain the highest degree of accuracy. Although stannate of soda containing an excess of hydrate of soda does not become turbid by boiling, as stated by Fremy, and the solution may even be evaporated until crystals separate, which entirely dissolve upon the addition of water, yet the antimoniate of soda contains a small quantity of oxide of tin. Consequently the sulphuret precipitated by sulphuretted hydrogen from the acid solution of the antimoniate of soda contains a small amount of sulphuret of tin, which does not part with the whole of its sulphur at the temperature

at which the sulphuret of antimony is reduced by hydrogen. For this reason a somewhat smaller amount of tin, a larger quantity of antimony, and a slight excess is found in the analysis.

On a new Method of estimating the Sulphur in Organic Bodies. *By* Dr. W. Heintz.

The author considers that the method proposed by Weidenbusch* does not afford perfect security against error, as a loss cannot be avoided when the organic substance is not completely oxidized; and moreover, the advantages of this method of oxidation over that by nitric acid are not satisfactorily proved; he therefore attempted to convert the whole of the sulphur into sulphuric acid by burning the organic substances with oxygen and oxide of copper. For this purpose an ordinary combustion-tube, open at both ends, was half-filled with copper turnings, and a little vessel containing dry pulverized taurine placed in the tube, which was then connected with a bulb-apparatus filled with solution of potash perfectly free from sulphuric acid, and the combustion made in a current of oxygen. The contents of the bulb-apparatus were now decanted into a spacious flask containing a warm solution of chlorate of potash in dilute nitric acid, and closed with a glass stopper. The sulphurous acid absorbed by the potash, and which had formed from the decomposition of a portion of the sulphate of copper, was by this means perfectly oxidized. The mixture of oxide, sulphate and metallic copper was treated in a beaker with the above mixture, and entirely dissolved at a gentle heat; the sulphuric acid precipitated by chloride of barium, and estimated as usual. As, along with the sulphurous acid, sulphuric acid always passes over into the bulb-apparatus, it is advisable, in order to avoid all loss of sulphuric acid, which might arise from condensation of the latter on the cork of the combustion-tube, to employ a tube which is drawn out at one extremity at a very obtuse angle into a fine tube, which fits into the stronger arm of a bulb-apparatus made for the purpose, and then connected with caoutchouc. The taurine examined yielded—1st, 25·68; 2nd, 25·66; and 3rd, 25·49 per cent. sulphur. Redtenbacher's formula, $C^4 H^7 NO^6 S^2$, requires 25·60 per cent. sulphur; the greatest error in the three experiments does not amount therefore to more than 0·11 per cent., which sufficiently proves the accuracy of the method. The combustion of the organic substance must not be carried on too quickly, otherwise a slight loss might readily occur from vapour passing through the solution of potash without being absorbed by it. It should be so conducted that no vapours are perceptible in the first bulb of the apparatus during the operation.—Poggendorff's *Annalen*, lxxi. p. 145.

* Page 215 of the present volume.

CHEMICAL PREPARATIONS.

On the Preparation of Valerianic Acid. *By* Dr. Aschoff.

On distilling 15 lbs. of valerian root with the addition of diluted sulphuric acid, according to the method described by Rabourdin, the author obtained 18 drms. $2\frac{1}{2}$ scruples of oily valerianic acid; and the aqueous liquid was still so strongly acid that it saturated several ounces of soda. In a second experiment the author obtained nearly the same result. The residue in the still was mixed with $4\frac{1}{2}$ oz. of sulphuric acid, and again distilled; the acid product saturated 5 oz. of carbonate of soda. After evaporation, the residue was mixed with a corresponding quantity of sulphuric acid, and then yielded on distillation $2\frac{1}{2}$ oz. of a mixture of acetic and formic acids. On separating these two acids by peroxide of mercury, the greater portion was found to consist of acetic acid. The amount of acetic acid is still further increased when the root is digested with water for 30 days previous to distillation; when, on the contrary, the root is placed for one or two days with water in a cool spot and then distilled, as large an amount of oily valerianic acid is obtained as in the first mode of preparation, and it is perfectly free from any foreign admixture. Most acid is obtained from the root gathered in the spring from dry localities after keeping a few months. When the whole of the valerianic acid has been removed by distillation of the root with water, the contents of the still always exhibit a strong acid reaction, arising from the presence of a resinous substance and free malic acid. The formic and acetic acids are combined with lime in the root; consequently an addition of acid is not to be recommended. The valerianate of ammonia which the author prepared could not be sublimed as stated by Riegel. It formed white feathery crystals, which only separated from the faintly-acid liquid, and melted at 89° F. without disengaging any ammonia; when heated still further, drops separated in the cold parts of the apparatus, but they assumed no crystalline form; when however the crystals were heated in an atmosphere of ammonia, crystals formed on cooling, which however deliquesced on exposure to the air. The acid appears therefore to form two compounds with ammonia.—*Archiv der Pharm.*, xlviii. p. 275.

On the Purification of Zinc. *By* M. Smedt.

Commercial zinc is dissolved in nitric acid; tin and antimony remain undissolved, the arsenic is converted into arsenic acid, and the zinc, cadmium and iron dissolve. Excess of carbonate of ammonia is added to the filtered solution, which precipitates the iron and the cadmium; the filtered liquid is evaporated to dryness, the residue heated to redness, dissolved in nitric acid, and the solution precipitated with carbonate of potash, which leaves the arsenic acid in the liquid; the precipitate is well washed, ignited, and then reduced at a red heat with hydrogen.—*Journ. de Chim. Méd.*, ii. p. 491.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Bile. By M. MULDER.

THE very extended investigation of the author commences with an examination of the results which have been made known by his predecessors on this point. The results of the author's investigations agree nearest with those of Berzelius, and extend chiefly to the study of the products of decomposition of the bile under different influences. An acquaintance with the labours of Berzelius, as also Gmelin, Kemp, Theyer and Schlosser, &c., is presupposed. They are collected in a monograph by Platner (Heidelb. 1845).

I. *Action of Muriatic Acid upon the Bile.*

The results of the following investigations show that the ultimate products of decomposition, which originate from old or fresh bile by the action of muriatic acid with heat, in addition to fats, colouring matters and salts, a little extractive, and some other slight admixtures, are essentially the three following:—

Taurine ..... $C^4 H^7 N O^6 S^2$
Ammonia ..... NH^3
Dyslysine ..... $C^{50} H^{36} O^6$.

Probably these three substances are the only ones which are formed from the bile by muriatic acid; for if the action of muriatic acid be not continued until dyslysine is formed, taurine, ammonia and fellinic and cholinic acids are the only products. The composition of these two acids is such that they may be regarded as $C^{50} H^{36} O^6 + n HO$. Hence the muriatic acid only causes the formation of taurine, ammonia and the hydrate of $C^{50} H^{36} O^6$.

If we examine bile fresh from the gall-bladder, we find in it taurine, ammonia and fellinic and cholinic acids; thus again $C^{50} H^{36} O^6 + n HO$. If we now decompose that part of fresh bile which does not belong to these substances by muriatic acid, we again obtain only taurine, ammonia and dyslysine, or fellinic and cholinic acid, according as the action has continued a longer or shorter time. Therefore taurine, ammonia and $C^{50} H^{36} O^6$, with or without water, are the entire products of the fresh bile. When

fresh bile is set aside, an extractive matter contained in it gradually disappears more and more, and at last entirely. In its stead, taurine, ammonia, dyslysine, fellinic, fellanic, cholanic and cholic acids appear in the same manner; these may all be referred to the formula $C^{50}\,H^{36}\,O^{6}$; so that we may regard the formula of dyslysine, $C^{50}\,H^{36}\,O^{6}$, as their prototype; which is also evident from the fact, that fellinic, cholinic, fellanic, cholanic and cholic acids all yield dyslysine, and nothing more, when heated with muriatic acid. When fresh bile, freed from fat and colouring matter and combined with bases, is burnt with oxide of copper, we obtain a mixture, which may be expressed by the constituents of taurine, ammonia and $C^{50}\,H^{36}\,O^{6} + n\mathrm{Aq}$.

When bile which has been kept longer, or even that which is perfectly putrid, is burnt, we obtain the same results.

Upon these reactions is based the conclusion, that the source of all the products of decomposition of the bile, the biline, should contain—

Taurine	$C^{4}\,H^{7}\,N\,O^{6}\,S^{2}$
Ammonia	$H^{3}\,N$
Dyslysine	$C^{50}\,H^{36}\,O^{6}$
Water	$H\,O$

as will be shown presently.

Biline cannot however be obtained in a state of purity. It is always procured in combination with one of the acids mentioned, which is moreover itself capable of combining with ammonia, the latter being simultaneously formed with one of the acids from the biline. Three such compounds may be distinguished—one with a minimum of biline, the second with a medium, and the third with the maximum.

The metamorphosis of the bile, which commences immediately after its secretion, and proceeds uninterruptedly, until at last no more biline remains, produces, as has been stated, ammonia. This remains with the soda; and the two retain, first the fellinic and cholinic acids, and subsequently the fellanic, cholanic and cholic acids in solution. All these acids are difficultly soluble in water, but form readily soluble salts with ammonia and soda. A certain quantity of the biline, during its metamorphosis, constantly yields enough ammonia to saturate the acid which is simultaneously formed. From this cause also the acids in decomposed bile always remain in solution; but the bile must then be regarded as a mixture of soda and ammonia salts, from which acetic acid can precipitate the acid. If this view is correct, ammonia must exist in perfectly fresh bile which contains fellinic acid; for when the fellinic acid originates from the biline, ammonia becomes free. In every examination of fresh bile ammonia was found; hence the fresh bile not only contains bilifellinate of soda, but also the ammonia salt of this acid.

When fellinate of ammonia is evaporated, a portion of the ammonia escapes, and the fellinic acid becomes insoluble in water. The same occurs with fresh bile. The fellinate of ammonia which it contains, and which is formed during its evaporation, loses ammonia

during the evaporation, and thus the bile becomes insoluble in water. The same also applies to cholinic acid.

It is thus evident that it is impossible to express the per-centage composition of the bile accurately, and therefore that we are ignorant of both its composition and equivalent. To ascertain the composition of the bile, we can only conclude with a certain amount of probability as to its constitution by accurately tracing its products of decomposition.

Decomposition of the Bile by Muriatic Acid.

If ox-bile be dried, dissolved in alcohol, and then decolorized with animal charcoal, on exhausting the mass again dried, it is found in a state no longer perfectly soluble in water. If the resinoid matter be then boiled several times with water, the liquids evaporated, and the residue boiled several times with muriatic acid, more of the resinous body is again separated. The only constituents which could be detected in the fluid in sufficient quantity to have any influence upon the composition of the bile, were chloride of sodium, ammonia and taurine, with phosphoric and sulphuric acids. Hence it appeared that the whole had become converted into the resinous bodies. The investigation of the changes which the entire bile undergoes by the influence of muriatic acid is difficult, on account of the soda contained in this fluid.

This resinous body might still contain dyslysine, fellinic and cholinic acids. Dyslysine is insoluble in cold alcohol, whilst the cholinic and fellinic acids are soluble in it. The former of these acids forms a barytic salt insoluble in alcohol; the latter, a soluble one. Fellinic acid is the first product of decomposition; on the further action of the muriatic acid, cholinic acid is formed; and by still further action, dyslysine. All three of these are different hydrates of $C^{50}\,H^{36}\,O^{6}$. The resinoid matter was soluble in alcohol even when cold. (I.) No dyslysine consequently was formed after three hours' action of muriatic acid upon the bile.

At the end of six hours but little was formed, but on boiling for twelve hours there was a considerable insoluble residue.

I. The resinous matter obtained on boiling for three hours with muriatic acid was finely powdered, perfectly freed from muriatic acid by water, and treated with ammonia. One portion dissolved, but another portion remained undissolved, part of it however passing through the filter with the former. After the separation had been effected as perfectly as possible, the dissolved portion (*a*) was evaporated to dryness. The undissolved portion (*b*) was also dried, and both saturated with barytic water. The excess of baryta was removed by carbonic acid, and the solutions of the salts evaporated to dryness, to treat them with alcohol when dried. *a* was entirely dissolved in the cold, *b* almost so. Both solutions were evaporated; *a* left about six times as much residue as *b*, which could only be fellinate of baryta. The insoluble portion could only contain cholinic acid and the carbonate of baryta. It was exhausted with muriatic acid, the residue then washed with water, dissolved in alcohol, and

the fluid evaporated. This could only be cholinic acid. Another portion of I., immediately after solution in alcohol, was treated with baryta in slight excess, evaporated to dryness, the residue exhausted with alcohol, and the fluid evaporated. The solution must again contain fellinate of baryta. The insoluble residue was treated with muriatic acid to separate the baryta, and freed from the latter by solution in alcohol; on evaporation the liquid yielded cholinic acid, the quantity of which however was but small.

II. When the resinous substance insoluble in alcohol, which had been boiled with muriatic acid for nine hours, was treated in the same way with baryta, it was found that the quantity of fellinate of baryta had diminished, whilst that of the cholinate had increased; hence a more prolonged treatment with muriatic acid converts the fellinic acid at first formed into cholinic acid.

Dyslysine.—By this name is understood a substance which is insoluble or difficultly soluble in boiling alcohol, is formed in the decomposition of the bile by muriatic acid, and was also found by Berzelius in the bile. But different substances are comprised under this term. If the action of the muriatic acid has not been continued sufficiently long, we obtain a very heavy substance, which is soluble in boiling alcohol, but is deposited from it on cooling. The composition of this substance exhibits a larger quantity of water. If the ebullition with muriatic acid has been continued for a longer time, the substance becomes deprived of water, and is then but slightly dissolved by alcohol, but very readily by æther. If the action of the acid be continued still longer, the substance then obtained is no longer soluble in æther. Hence there are three kinds of dyslysine. That soluble in æther is $C^{100}\,H^{73}\,O^{13}$; that deposited from boiling alcohol is $C^{100}\,H^{74}\,O^{14}$.

Dyslysine obtained by boiling the decolorized bile with muriatic acid, and which was insoluble in alcohol but soluble in æther, was of the composition *a*. The other two analyses represent dyslysine prepared from biline, or that portion of the bile not precipitable by basic acetate of lead:—

	a.			Atoms.	Calculated.
Carbon	77·12	77·14	77·10	100	77·26
Hydrogen	9·56	9·22	9·22	73	9·37
Oxygen	13·32	13·64	13·68	13	13·37

When the following remarks are also taken into consideration, it is probable that the dyslysine soluble in æther consists of $C^{50}\,H^{36}\,O^{6}$.

The results obtained by analysis differ from this formula by half an equivalent of water; they give $C^{50}\,H^{36}\,O^{6} + \frac{1}{2}$ aq. Hereafter $C^{50}\,H^{36}\,O^{6}$ is assumed as the expression, for the sake of elucidating the relations of the other substances. The portion which had subsided from the spirit on cooling was washed with cold alcohol, and was perfectly soluble in ether. It yielded—

	Found.		Calculated.
Carbon	76·68	100	76·38
Hydrogen.....	9·76	74	9·39
Oxygen.....	13·56	14	14·23

These results correspond to the formula $C^{50}\ H^{36}\ O^{6} + H\,O$. Dyslysine must therefore in future be separated into two or three substances :—

$$C^{100}\ H^{72}\ O^{12}\ (?)$$
$$C^{100}\ H^{73}\ O^{13}$$
$$C^{100}\ H^{74}\ O^{14}$$

We must not however consider every deposit which falls from boiling alcohol as dyslysine; for these frequently consist of a mixture of cholinic acid and dyslysine. The dyslysine may also contain taurine, and must therefore be boiled with water if required pure.

Fellinic and Cholinic Acids.—It is very difficult to obtain these two acids in a pure state, as they are very difficult to separate from each other. Moreover, we frequently find, when the greater portion consists of fellinic acid, that it is contaminated with bilifellinic acid and taurine. These substances are best purified by rubbing them into a fine powder, and washing this with water; when, if it contains bilifellinic acid, a milky fluid is obtained, which cannot be rendered clear by filtration. In this case the substance must be again boiled with muriatic acid. When it has been well washed with water, it is dissolved in absolute alcohol and allowed to cool. Taurine is then deposited. But the bilifellinic acid is never then perfectly separated; and a resinoid substance of this kind may yield 70 per cent. carbon on combustion; the presence of sulphur and nitrogen then indicates the admixture of biline.

On the analyses of these substances, the following results were obtained. Thus, that portion of the resinous matter which was obtained by three hours' boiling, and was soluble in alcohol, after having been evaporated to dryness with barytic water and treated with alcohol, may still consist of a mixture of fellinic and cholinic acids, and is therefore not adapted for the determination of the atomic weight. This baryta salt, when dried at 248°, yielded 18·21 per cent. of baryta. On combustion with chromate of lead, it yielded—

			Calculated.
Carbon	72·79	100	72·24
Hydrogen	9·97	79	9·48
Oxygen	17·24	19	18·28

or $C^{50}\,H^{36}\,O^{6} + 3\tfrac{1}{2}HO$.

The organic matter was separated from this barytic salt by muriatic acid, and the chloride of barium removed by washing with water until the substance when incinerated left no trace of ash. The pure organic matter now yielded—

	I.	II.
Carbon	72·10	72·01
Hydrogen	9·68	9·72
Oxygen	18·22	18·27

Now this substance was a mixture of fellinic and cholinic acids; the barytic salt appears to contain less water, as the carbon came out somewhat higher in it than in the free acid.

The barytic salt was purified in the following manner:—It was dissolved in the smallest quantity of alcohol possible, and set aside for some days. During this time cholinate of baryta separates. The alcoholic solution is poured off clear, filtered, and evaporated to dryness; it evidently contains a much purer fellinate of baryta. When dried at 266° F., it yielded 10·15 per cent. of baryta. However, even this salt could not be considered as sufficiently pure to allow of our determining the equivalent of the organic matter from it. On ultimate analysis it yielded—

Carbon	72·63
Hydrogen	9·96
Oxygen	17·41

Thus the composition of the organic matter was not perceptibly altered by this separation of it from the cholinate of baryta; and hence it was impossible to separate these acids perfectly by this method, or fellinic acid must differ but little from cholinic acid.

The resinoid mixture formed by boiling for three hours was dissolved in excess of ammonia by heat; and, although it was somewhat turbid, precipitated with nitrate of baryta, and the precipitate separated by filtration washed with water. By this process some fellinate of baryta is dissolved. If it still contains any bilifellinic acid, this must also exist in the washing water. The washed precipitate was treated with cold spirit; it concreted, and the fluid remained turbid. The latter was poured off the glutinous cholinate of baryta, and the spirit evaporated. The residue now contains the fellinate as free as possible from cholinic acid, although it cannot even now be regarded as perfectly pure. Dried at 266°, it gave 8·72 per cent. baryta, and—

Carbon	72·98
Hydrogen	9·80
Oxygen	17·22

To separate the cholinic from the fellinic acid, the above method by the separation of the barytic salts was adopted. The cholinic acid could not however be obtained sufficiently pure for the atomic weight to agree accurately with its composition. It will therefore only be mentioned here, that the so-called choloidic acid is in fact at least of three kinds; that with ammonia and water it yields a soluble and an insoluble salt; that the insoluble salts of baryta and ammonia contain an acid in which the amount of carbon is more than in fellinic acid and less than in dyslysine; moreover, that it is very readily converted into one or the other, with either the liberation or absorption of water, without any other compound being formed; again, that its composition, as it occurs in an acid salt, may be expressed by the formula $C^{100}H^{77}O^{17}$, and that this acid, Berzelius's cholinic acid, in the anhydrous state consists of $C^{50}H^{38}O^{8}$; and, in comparison with dyslysine, $C^{50}H^{36}O^{6} + 2HO$ appears to be a hydrate.

Notwithstanding the atomic weight of cholinic acid could not be ascertained with sufficient accuracy, that of fellinic acid may be

regarded as determined with tolerable certainty. Its formula in the anhydrous salts is $C^{50}H^{40}O^{10}$, and in the hydrated state $C^{50}H^{40}O^{10} + HO$. Its per-centage composition is as follows:—

	Found.	Calculated.
C^{100}	70·73	70·71
H^{81}	9·78	9·52
O^{21}	19·49	19·77
	100·00	100·00

The formula of the barytic salt, which according to the above requires 8·25 per cent. baryta, also agrees with the results of experiment, 8·19 per cent. being the amount obtained. The composition of this salt therefore appears to be determined with sufficient accuracy as $2(C^{50}H^{40}O^{10}) + HO + BaO$. Hence the anhydrous fellinic acid, on comparison with dyslysine, would be—

$$C^{50}H^{36}O^{6} + 4HO.$$

Moreover, the resinoid body, which was boiled with muriatic acid for nine hours, was treated with barytic water, evaporated, and the residue exhausted with cold spirit. The portion dissolved must consist of fellinate of baryta, which might however contain some cholinate of baryta. The fellinate was dried at 266° F. It yielded 16·09 per cent. of baryta, and—

			Calculated.
Carbon	71·96	50	71·48
Hydrogen	9·50	40	9·50
Oxygen	18·44	10	19·02
			100·00

The formula requires 15·5 baryta.

Fellinic acid may therefore be regarded as $C^{50}H^{40}O^{10}$, and cholinic acid as $C^{50}H^{38}O^{8}$, although the latter was not checked by the estimation of its equivalent.

If we start with dyslysine, we have the following empirical expressions:—

Dyslysine	$C^{50}H^{36}O^{6} + \frac{1}{2}HO$
Cholinic acid	$C^{50}H^{36}O^{6} + 2HO$
Fellinic acid	$C^{50}H^{36}O^{6} + 4HO$

which also give an insight into the mode of transformation of one compound into the other. These formulæ are moreover confirmed by the analyses which were made upon the mixtures of these bodies. One of these has been previously detailed, the composition of which was $= C^{100}H^{79}O^{19}$, or $= C^{50}H^{36}O^{6} + 3\frac{1}{2}$ aq, which is thus intermediate between that of fellinic and cholinic acids.

Demarçay found the following as the composition of the mixture of the two acids (C = 76·437):—

			Dumas and Pelouze.	
Carbon	73·52	73·30	73·16	73·3
Hydrogen	9·58	9·51	9·48	9·7
Oxygen	16·90	17·19	17·36	17·0

and his choloidic acid is also this mixture of fellinic and cholinic acids. If the results are calculated for C = 75·12, we obtain—

Carbon.....	100	72·24	$= C^{50} H^{40} O^{10} - 1aq.$
Hydrogen	79	9·48	
Oxygen	19	18·28	

hence exactly the same result as was obtained above for the mixture of fellinic and cholinic acids.

According to the author, it is moreover probable that the acid obtained by Theyer and Schlosser by means of oxalic acid, was fellinic acid, since the mean of the numbers obtained by them, when compared with the formula $C^{50} H^{40} O^{10}$, approximate to this. For as the silver salt and the lead salt could not be neutral, because the former was procured from evaporated fellinate of ammonia, which gives off ammonia during evaporation, and the latter was prepared by the double decomposition of acetate of lead with fellinate of potash, and hence might well be sesquibasic, the atomic weights found, viz. 6051 for the silver salt and 3362 for the lead salt, must be multiplied.

Berzelius found, what the author confirms, first, that a spirituous solution of potash converts dyslysine into cholinic acid and the latter into fellinic acid. If this solution be boiled for a considerable time, the spirit being constantly replaced until all the dyslysine is dissolved, the alcohol then be evaporated, and precipitation be produced by muriatic acid, if the boiling has not been continued too long, we obtain cholinic acid, but on more continued ebullition, fellinic acid and dyslysine. This explains more minutely the simple relation of these three bodies; we see that the muriatic acid constantly removes water, which the alkali replaces. The properties of the substances which have been examined are given below, to allow of their comparison with those described by Berzelius. They are all three free from nitrogen.

Dyslysine.—Resinous, white and pulverizable, very difficultly soluble in alcohol, readily so in æther, insoluble in water and tasteless. When heated with an alcoholic solution of potash, it is resolved first into cholinic acid, and then into fellinic acid; and these acids can then be separated from the alcoholic solution. The intimate connection between fellinic and cholinic acids and dyslysine is here still more evident than on the decomposition of fellinic acid into cholinic acid, and of these two into dyslysine by the action of muriatic acid.

Cholinic Acid exists in the bile in much less quantity than fellinic acid, is produced from the latter on strongly drying, and is restored by potash in a spirituous solution with heat into fellinic acid. It is white, pulverizable, fuses like a resin, and melts in hot water; is soluble in alcohol, but not so readily as fellinic acid. It is but little soluble in æther. It is a weak acid, and has a bitter taste.

The neutral ammonia salt loses ammonia on drying. The barytic salt is insoluble in water, almost insoluble in spirit, but is dissolved by fellinate of baryta.

The lead salt is insoluble in water and spirit. Cholinic acid combines with biline, forming bilicholinic acid, which, when it contains much biline, is soluble in barytic water.

Fellinic Acid is white, pulverulent, of a bitter taste, melts in boiling water, and is slightly soluble in it; it is more soluble in æther, readily so in spirit, and this solution has an acid reaction. It is soluble in alkalies, and acetic acid throws it down from these solutions as a white precipitate. It is insoluble in barytic water, but becomes soft in it, and the barytic salt is readily soluble in spirit.

The lead salt is insoluble in water. It combines with biline in different proportions, and then forms soluble salts with baryta and insoluble salts with lead.

Cholanic Acid has not been further examined.

Fellanic Acid is white, pulverulent, of a bitter taste, melts in boiling water, and is readily soluble in alcohol and æther. It exists in stale bile, and forms with alkalies salts which are soluble in water, as it does also with baryta and neutral salts of lead. It is readily formed from fellinic acid.

Cholic Acid was not examined.

The obstinacy with which fellinic, cholinic and fellanic acids retain spirit is remarkable. At ordinary temperatures the spirit cannot be driven off, but when kept at an elevated temperature for a very long time, this is effected. The spirit therefore appears to combine with the acids, and it may readily give rise to errors in analysis. The same holds good with the bile and the salts of these acids; they also retain a considerable quantity of spirit, which they only part with when heated for a long time.

[To be continued.]

On the Presence of Fluorine in Anthracite.

By George C. Schaeffer.

But little attention has hitherto been paid to the curious pseudo-sublimate formed in the flues of stoves in which anthracite coal is burned. Several years ago a committee of the Franklin Institute made a report on the corrosion of iron pipe, &c. by the burning of anthracite. This is the only notice of this substance known to us. The committee attributed the corrosion to the action of ammoniacal salts containing sulphuric acid and chlorine.

The substance in question is not wholly a sublimate, being formed partly by the condensation of ammoniacal salts, and partly by the direct action of the gaseous products of combustion on the iron; when the fire has been frequently rekindled, there is more or less mixture of carbonaceous matter.

The action of damp air on this substance when cold increases the corrosion of the pipe, as demonstrated in the report above-mentioned. This however is not the *sole* cause, for large flakes may easily be separated from pipes which have not been exposed to damp air, and these will always be found to contain much iron.

There is another substance found in the pipes; this is formed of

the ashes carried up by the draught, and is more or less encrusted and mixed with the condensed products of combustion.

Soon after the report of the Committee of the Franklin Institute was published, my attention was drawn to the same subject. I found, on subliming even the smallest portion of these flakes in an open glass tube, that the glass was corroded. As I was engaged in determining the presence of another substance, I did not pay much attention to this indication of the presence of fluorine.

I have more recently tried the usual test for fluorine, and find that with a small quantity of the sublimate the glass is always engraved; even a few grains will suffice to give marks which are visible when the glass is dimmed by breathing on it*. This reaction uniformly takes place; and we may therefore add fluorine to the number of elements already found in anthracite.

Since making these experiments, my attention has been directed to a note by the Messrs. Rogers, on the occurrence of fluor spar in anthracite; these gentlemen correctly attribute the fluorine to the vegetation of the coal plants, although no attempt seems to have been made to determine its constant presence in the coal.

A single trial has shown that phosphoric acid is likewise present. I have not repeated the experiment, but there can be no doubt that this constituent of plants of our æra was equally abundant in the coal plants.

It may be remarked, that the sulphur is not altogether found as sulphuric acid in the sublimate, for hydrochloric acid disengages a large quantity of sulphurous acid. The investigation of this curious substance is not yet completed. The results, if worth recording, will be communicated to this Journal.—Silliman's *Journal*, May 1847.

On the Balsam of Tolu and some Products obtained from it. *By* E. Kopp.

The composition of the balsams of Tolu and Peru has been established by the researches of M. Plantamour and by the beautiful investigations of MM. Fremy and Deville. M. Deville also examined the products of the destructive distillation of the balsam of Tolu, and we are indebted to him for the discovery of benzoene and its derivatives, substances analogous to benzine; one of these derivatives, nitrobenzoene, has been transformed by Muspratt and Hofmann into a remarkable artificial alkaloid, toluidine. My experiments confirm the greater part of the results already obtained. The balsam of Tolu is composed of—

1. A very small quantity of tolene, $C^{10} H^8$ ($C = 75$ $H = 6{\cdot}25$).
2. Free cinnamic acid, $C^{18} H^8 O^4$.
3. A resin very soluble in alcohol, $C^{36} H^{19} O^8$.

* If the leaden vessel in which this experiment has been tried is allowed to stand for some time, a large quantity of transparent and perfect octahedrons of iron and ammonia alum will be found. These may be readily freed from the black residue by agitation with a small quantity of water. The crystals however soon become opake and brown when exposed.

4, A resin but little soluble in alcohol, $C^{18}H^{10}O^5$, or rather $C^{36}H^{20}O^{10}$.

1. *Tolene.*—This carburet of hydrogen was prepared exactly according to the method proposed by M. Deville. It is colourless, very fluid, of a pungent and slightly peppery taste, and possesses an odour resembling that of elemi. Its specific gravity at 50° F. is 0·858, and its boiling-point between 309° and 320° F. When set aside in an imperfectly-closed tube, it gradually becomes resinified and very slightly coloured. M. Deville assigned to it the formula $C^{12}H^9$. My analyses, which differ but little from those of M. Deville, agree better with the formula $C^{10}H^8$, which also corresponds with the boiling-point.

2. *Cinnamic Acid.*—The free acid of the balsam of Tolu is cinnamic acid only, as M. Fremy had observed. This fact was proved by analysis and by the conversion of the acid into nitrocinnamic acid, which is but very slightly soluble in cold alcohol, whilst benzoic and nitrobenzoic acids are very soluble in it.

The results obtained by M. Deville probably arise from his having examined the acids obtained by the distillation of the balsam, or extracted by concentrated alkaline solutions. I have proved that under these circumstances the resins of the balsam of Tolu become transformed in such a manner as to give rise to the formation of a large proportion of benzoic acid. The resins, carefully distilled with caustic soda, yield pure benzoene and a carbonaceous residue, containing a considerable quantity of benzoate of soda (the boiling-point of protonitrobenzene is 446° F.). Cinnamic acid, when mixed with concentrated and cold caustic soda, and exposed to a current of chlorine, becomes transformed into chlorocinnamic acid, $C^{18}(H^7Cl)O^4$. However, if the temperature is high and the reaction violent, the chlorinated oil noticed by Stenhouse is disengaged, and chlorobenzoic acid formed. These two acids resemble each other considerably, but the latter is more soluble in water and alcohol, and the salts crystallize more readily. It is also obtained from benzoic acid, caustic soda and chlorine. Cinnamic acid, when treated with concentrated nitric acid, is at first transformed into nitrocinnamic acid, then into benzoic acid, and finally into nitrobenzoic acid.

Cinnamic and benzoic æthers also become transformed, but with more difficulty, into nitrocinnamic and nitrobenzoic æthers. A great portion of the æther is almost always decomposed and the acids set free. Nitrobenzoic æther is solid, colourless, and of an aromatic taste and odour. It crystallizes in beautiful laminæ, belonging to the right prismatic system. Its fusing-point is 116° F., and its boiling-point 564°. It is easily obtained by subjecting an alcoholic solution of nitrobenzoic acid to a current of muriatic acid. Its formula is $C^{14}(H^4NO^4)O^3 + C^4H^5O = C^{18}H^9NO^8$. Nitrocinnamic acid, dissolved in an alcoholic solution of sulphuret of ammonium, is reduced with the aid of a slight elevation of temperature. Sulphur is deposited, and two distinct matters are formed, one of which, of a yellow madder colour, belongs to the class of

resins, and the second to the class of alkaloids. The latter is solid, colourless, crystallizable in warts, insoluble in water, soluble in alcohol and æther, and forms difficultly crystallizable salts.

Resin α. $C^{36} H^{19} O^8$.—This is brown, translucid, brittle when cold, and shining; its powder agglomerates at 59°, and fuses completely at 140° F. Concentrated sulphuric acid colours it purple. When dissolved in caustic potash and exposed to the air, it easily becomes oxidized and transformed into the resin β. On dry distillation it yields benzoene and benzoic acid. It readily dissolves in alcohol and æther.

Resin β. $C^{18} H^{10} O^5$.—Dull yellowish-brown, neither taste nor smell, slightly fusible (above 212° F.), but slightly soluble in alcohol and æther; less easily altered than the preceding resin. Sulphuric acid colours it violet-red; caustic potash dissolves it with a brown colour.

The mixture of the two resins, when treated with nitric acid, yields gaseous products, consisting of carbonic acid, nitrous vapours and deutoxide of nitrogen; volatile products, consisting of the hydruret of benzoyle, hydrocyanic and a little benzoic acids; and as a residue, a flaky yellow matter, which consists of benzoic acid, intimately combined with a yellow resinous colouring matter, which prevents it from crystallizing, and accompanies it in all its combinations, even in that with æther. By the action of heat, especially by distillation, the resinous matter is destroyed, and the benzoic acid is obtained in a perfectly pure state; the resin furnishes nearly the third of its weight of benzoic acid.

The constitution of the balsam of Tolu seems very simple.

Originally the balsam is formed by the soft resinous matter $C^{36} H^{19} O^8$, or that which gives rise to it. This resin, under the influence of the air, becomes converted into cinnamic acid and the resin β, $C^{36} H^{19} O^8 + O^2 = C^{18} H^8 O^4 + C^{18} H^{10} O^5 + HO$. We observe, in fact, that in time the balsam of Tolu becomes hardened, and contains a larger quantity of cinnamic acid.

The resin $C^{18} H^{10} O^5$ can of itself easily yield benzoic acid, for $C^{18} H^{10} O^5 = C^{14} H^6 O^4 + 2HO + C^4 H^2$. Perhaps the tolene is derived from the carburetted hydrogen; but it is more probable that it becomes converted into a resinous colouring matter, or into water and carbonic acid, by the action of oxidizing bodies*.—*Ann. de Chim. et de Phys.*, July 1847.

On the Fatty Acids of Cocoa-Nut Oil. *By* St. Evre.

The products resulting from the saponification of crude cocoa-nut oil yield large but variable quantities of oleic acid and glycerine.

* The presence of muriatic acid in the nitric acid singularly promotes the formation of oxalic acid. The resins of benzoin and Tolu do not yield oxalic acid when treated with pure nitric acid. It is obtained however when an impure acid is used. Pure nitric acid gives rise to terebic acid by reacting upon the oil of turpentine, and oxypicric acid, by oxidizing the gum-resins. On employing nitric acid containing a considerable quantity of muriatic acid, we obtain only oxalic acid under the same circumstances.

The glycerine, isolated in the usual manner, exhibits the known properties, is neutral, dissolves in sulphuric acid, and furnishes acroleine on dry distillation. The oleic acid is oily, and yields on destructive distillation a considerable quantity of a substance which dissolves in boiling water, crystallizes in pearly laminæ, melts at 257° F., and possesses the composition of sebacic acid. It gave on analysis 59 C, 9·04 H, and 31·66 per cent. O, which corresponds to the formula $C^{10} H^{9} O^{4}$. But since oleic acid has the property of dissolving other fatty acids, it had to be proved that the oleic acid was perfectly pure. From the boiling-point found by Bromeis, the acid should have, according to Dumas, the formula $C^{22} H^{22} O^{4}$, instead of $C^{27} H^{27} O^{4}$, that arrived at by Bromeis. It is probable therefore that what he examined was a mixture of several fatty acids; the oil was consequently pressed between paper and repeatedly crystallized; the solid *cocinic acid* which remained gave—

Carbon	73·94	72·67	72·44	71·60
Hydrogen	11·87	11·92	12·05	12·07
Oxygen	14·19	15·41	15·51	16·33

As the last analysis, for which the substance had been again purified, furnished a lower amount of carbon, the author concluded that it must still contain oleic acid; he therefore prepared the lead salt, and digested it with æther, in order to remove entirely the oleic acid. When cocinic acid is precipitated from its hot alkaline solutions, a volatile oily vapour is disengaged, which smells strongly of Chevreul's phocenic acid. The acid was now crystallized from alcohol, and obtained in the form of warty crusts; it was then saturated with soda, dissolved in alcohol, and precipitated with a solution of acetate of lead; the magma which results is digested for several days with æther; the residue, which is decomposed in boiling water with tartaric acid, gives very pure cocinic acid, which only requires to be dissolved in alcohol and crystallized. Cocinic acid crystallizes in colourless stellately-grouped needles, melts at 94°, and dissolves readily in æther and alcohol; it is perfectly void of smell, and forms, after being fused for a long time and then cooled *in vacuo*, a colourless, hard, friable mass. It is volatile, but only in a current of gas. From 600 grms. of cocoa-nut oil, the author did not obtain more than 7 to 8 grms. of pure acid, which gave on analysis—

Carbon	70·97	70·88	70·90	22	=	132	70·96
Hydrogen	11·88	11·88	11·89	22		22	11·82
Oxygen	17·15	17·24	17·11	4		32	17·20

Cocinic Æther forms a light yellowish fluid, which has the fragrant odour of apples, and an insipid, sweetish taste. It is easily obtained in the usual manner, by passing a current of muriatic acid gas through a hot alcoholic solution of pure cocinic acid, when the æther soon separates; it is washed first with pure, and then with faintly-ammoniacal water, and finally digested with fused chloride of calcium. The analysis yielded—

Carbon.....	73·15	72·83	26 =	156	72·86
Hydrogen	12·22	12·18	26	26	12·14
Oxygen	14·63	14·99	4	32	14·97

The rational formula is $C^{22}H^{21}O^3$, C^4H^5O.

Cocinate of Silver is obtained from alcoholic solutions by double decomposition; it dissolves readily in æther, sparingly in alcohol, melts at 131°, and forms while fresh snowy white flakes. It gave on analysis—

Carbon	44·85	..	..	22 =	132·00	45·04
Hydrogen	7·29	..	..	21	21·00	7·17
Silver.....	36·59	36·66	36·77	1	108·04	36·86
Oxygen	11·27	..	..	4	32·00	10·93

The author endeavoured to obtain cocinone by distillation of the lime salt. The lime salt is white, amorphous, and melts at a low temperature; it yielded on distillation a light residue and a pale yellowish liquid, which appeared to undergo some change on boiling, but, from want of material, could not be examined more in detail. One analysis yielded 79·73 C and 12·90 per cent. H, which corresponds to the formula $C^{21}H^{21}O$.—*Ann. de Chim. et de Phys.*, xx. p. 91.

Chemical Examination of some Objects of Antiquity.
By M. Girardin.

Antique Solder.—The substance examined was found in a tomb which dated from the third century. It consisted of sand, which however must be regarded as an impurity, and of lead, of which a part was converted into carbonate. The ordinary lead-solder consists of an alloy of tin and lead; but quite recently it has again become the practice to use pure lead for the purpose.

Two Axes.—These were both of bronze; the one, Roman (I.), was discovered in the forest of Roumare; the other (II.) was Gallic, and was discovered in the neighbourhood of Elbœuf. The latter was reddish, easily filed, and very brittle. They contained—

	I.	II.
Copper	77·77	74·9
Tin	19·61	25·1
Zinc.....	1·44	
Lead	1·18	

It is seen from this, as well as from former analyses, that the ancients made their bronze in various ways, and of materials of very different purity.

Antique Copper Vessel.—This was found in a Roman tomb, and was at first considered to be bronze; but on closer examination it was found to consist of pure copper, coated internally with an alloy of 68·88 parts of tin and 31·12 parts of lead. There was no silver or zinc to be found in it. The tinning of copper vessels was first discovered by the Gauls; but Pliny does not state whether they did it to ornament the utensils or to prevent the formation of verdigris.—*Journ. de Pharm. et de Chim.*, x. p. 321.

On the Preparation of the Cyanide of Potassium.
By C. Clemm.

When an intimate mixture of 8 parts of anhydrous ferrocyanide of potassium and 3 parts of dry carbonate of potash is heated in a covered iron crucible until the fused mass is faintly red-hot, has become clear, and a sample, taken out and allowed to cool, appears perfectly white, the whole of the prussiate is reduced. If the crucible be now removed from the fire, the evolution of gas ceases, and the eliminated iron is very soon deposited, especially when the crucible is gently tapped, so that with a little care the greater portion of the cyanide of potassium can be poured off the iron. To obtain it perfectly free from iron, it is best to strain it through a hot iron spoon, pierced with fine holes, into a tall vessel of silver, iron or porcelain, with smooth sides, which is placed in a warm spot, that the fused mass may cool slowly. The lower portion, containing the iron, may be readily removed with a hammer. The purity of the cyanide of potassium depends on the purity of the materials used; above all, the carbonate of potash should be free from sulphate; otherwise the sulphur passes in the form of sulphuret of potassium into the cyanide, and thus partially prevents its application in analysis. If the above mixture be fused until the mass flows quietly at a bright red heat, the preparation is generally coloured gray. On dissolving some of this gray cyanide, perfectly free from particles of iron, in cold water, it leaves on filtration a black body, which burns entirely upon platinum foil, and presents all the properties of carbon. This finely-divided carbon can no longer be removed from the cyanide of potassium by fusing it again and allowing it to settle, owing to its low specific gravity. It may be added to a fresh preparation without doing any harm, as the eliminated iron appears to carry down with it the finely-divided carbon.—Liebig's *Annalen*, lxi. p. 250.

ANALYTICAL CHEMISTRY.

On Poisoning by Vegetables, or their Proximate Principles in general, and by Opium or Morphine in particular. By M. Ch. Flandin.

This memoir is divided into two parts. In the first, the author proposes two new analytical processes, both based upon the two following experimental facts,—1st, that the proximate principles of poisonous vegetables, such as morphine, narcotine, brucine, strychnine, &c., are not decomposed when in contact with animal matters at a temperature of 212° F., or a few degrees above it; 2nd, that ammonia precipitates the vegetable alkalies from their acid solutions when present to the extent of a thousandth part and less.

The two processes have this in common, that at first, whatever the matters for analysis may be, they must be dried in a sand-bath

at a temperature not exceeding 239° F. They are then broken up, and afterwards powdered in a machine described in the first volume of the author's 'Traité des Poisons,' p. 414.

The matter thus prepared is treated, according to the more or less dry or coagulable state of the products, either with water acidified with 0·025–0·05 acetic acid, or with absolute alcohol, to which, according to the nature of the proximate principle to be sought for, a small quantity of powdered oxalic or tartaric acid is added. This addition of acid, which can, or rather ought to be made either before or after the treatment with alcohol, serves to transform the vegetable alkaline base into an extremely soluble salt or supersalt; because this salt has to be subsequently taken up by cold water, so that the base may be precipitated by ammonia.

In the analysis of the urine, the treatment must be special; but it is easily described. The liquid should be evaporated to the consistence of an extract, this completely dried by adding powdered alumina, and the solid, when perfectly pulverized, treated with cold water acidified with 0·02–0·05 acetic acid. The solution is precipitated by ammonia, the precipitate washed and collected.

In using these processes, it is no longer the extracts of animal matters which are subjected to the chemical reactions adopted for detecting the vegetable bases sought for; these bases are obtained in a pure state, or in the form of crystals. The author uses a small peculiar filter, described by M. Danger, by which the smallest quantity of any precipitate may be collected without loss, which is of great importance in delicate researches like the present*.

In the second part of the memoir, the author has applied the preceding researches to the study of opium, or rather one of its immediate principles, morphine. He has given various compounds of this base to several species of animals, cats, dogs, rabbits, birds, and a monkey.

An important fact resulting from these experiments is, that morphine is tolerated in enormous doses by the above animals. Is not this poisonous base decomposed, neutralized by the gastric fluids, under the influence of the vital force? It is known, on the one hand, that morphine is decomposed by certain powerful acids, *e. g.* nitric acid; the author has shown, on the other hand, that the same decomposition is produced by the action of a chloride or alkaline hypochlorite and a weak acid; the chloride of lime and the hypochlorite of soda produce this effect when acetic, oxalic and tartaric acids, &c. are present or act as intermediate agents. The result of the latter decomposition furnishes a new reaction, which must be added to the most characteristic chemical reactions of the alkaline vegetable bases. Thus morphine, under these circumstances, yields a fine yellow colour; narcotine, a red colour; brucine, a rose-red colour; whilst strychnine undergoes no change. There is nothing therefore which should occasion surprise in the fact, which the author thinks he has established by direct experiments, viz. that morphine

* See Traité des Poisons, &c., p. 397.

may be decomposed or burnt during the process of digestion or the act of respiration.

But, admitting this to be the case, it is not less true, that according to the doses taken, the whole of the morphine is not suddenly transformed or destroyed, either in the digestive canal or in the torrent of the circulation. The author has found this poisonous substance in the fæces of the animals; also in their urine, and even in their internal viscera. Thus, in the case of a monkey, which for thirty days underwent a course of this substance, and during this interval took 30 grms., or an oz. of morphine, a decigramme was obtained in crystals from the urine. The author sums up in the following proposition:—The vegetable poisons, especially morphine, are capable of being partly neutralized when mixed with the vital fluids or exposed to the influence of the vital forces; but the portion which produces the morbid effects, the portion which kills, remains undecomposed in the organs, and chemistry is capable of detecting it.

This proposition appears to involve an extremely interesting consequence. Infanticides produced by substances called *abortive* are real cases of poisoning, which may be confined to the product of conception, just as they may sometimes extend to the mother. Strictly speaking, all poisons, according to this view, are abortive substances. The poisonous substance is, as it were, directly transported to the organs of conception by absorption, the uterus, during pregnancy, by means of its peculiar function, exerting a kind of eliminating power. A small dose, incapable of killing the mother, suffices to destroy the fœtus; and when this is dead, abortion is the consequence.

In making experiments upon the mineral poisons, and especially arsenic, the author has seen rabbits abort, and found the poison in the young ones. These experiments have been renewed in studying the effects of morphine. Two rabbits which had taken the poison with their food aborted, as did also a bitch poisoned by subcutaneous absorption. Unfortunately, these experiments could not be made complete or conclusive; for the rabbits devoured almost all their little ones, and the bitch ate the placentæ in her case. The author thinks it highly probable that, as in the case of arsenic, the poisons reach the products of conception, and that chemistry may discover them when used as instruments of crime in cases of abortion; moreover, that poisoning is a phænomenon of absorption, and that the agent of crime remains in those parts where it has produced its pathologic or mortal effects.

The author also proposes the use of weak acids, mixed with chlorides or alkaline hypochlorites, as antidotes to morphine, narcotine and brucine. The vegetable acids have been considered as counter-poisons to opium and the vegetable alkalies in general. Chemically speaking, the dilute vegetable acids are very powerful solvents of the proximate principles, as morphine, narcotine and brucine. Are they not counter-poisons merely because they meet with alkaline chlorides in the œconomy? As necessary adjuvants to these acids, it would then be very useful to conjoin the special chlorinated com-

pounds which have been mentioned. These theoretical inductions must however be confirmed by experience.—*Comptes Rendus*, July 26, 1847.

On the Occurrence of Arsenious Acid and other Metallic Oxides in Mineral Waters, and their Quantitative Determination. By Dr. H. Will.

Owing to the observations of Tripier, Walchner and others, much attention has recently been directed to the presence of arsenic and other heavy metals in mineral waters; and the author has likewise succeeded in demonstrating the presence of arsenic, copper, lead, tin and antimony in the springs of Rippoldsau. Other ochreous deposits examined by the author constantly exhibited the presence of metals; arsenic and tin, in fact, were never absent. In the sediments formed at the sources, as well as in the water itself, the arsenic exists in the state of arsenious acid, the tin in the form of protoxide. If the well-washed ochre from the springs of Rippoldsau or Wiesbaden is boiled, for instance, with pure solution of caustic potash, filtered, and the filtered solution, after being cautiously neutralized with nitric acid, treated with nitrate of silver, a yellow precipitate is obtained; and if the muriatic solution of the ochre is mixed with sulphurous acid, a brownish-yellow precipitate of sulphuret of tin results. In the qualitative determination of the above metals, it is always advisable to heat the muriatic solution of the sediment with sulphurous acid until the whole of the peroxide of iron is converted into protoxide, and the odour of sulphurous acid has again entirely disappeared, previously to passing sulphuretted hydrogen through it; otherwise so much sulphur falls with the metallic sulphurets, that the detection of the arsenic is rendered far more difficult. To estimate the quantities, an indefinite weight of the sediment, or of the insoluble portion of the residue on evaporation, was digested with a large quantity of water and some muriatic acid until nothing further dissolved; the clear solution warmed with an excess of sulphurous acid, and sulphuretted hydrogen passed through it to saturation. The brownish-yellow precipitate, consisting of the metallic sulphurets, was collected on a weighed filter, dried at 248° F., and weighed. In one portion of the precipitate the amount of sulphur was estimated by oxidation with nitric acid and precipitation by barytes. By deducting the sulphur, the amount of the collective metals contained in the ochre for a certain weight of peroxide of iron was ascertained. The peroxide of iron was carefully separated from alumina, &c., according to the usual methods. Another portion of the weighed sulphurets was digested with the hydrosulphate of potash, when sulphuret of arsenic, sulphuret of antimony and sulphuret of tin were dissolved, while the sulphurets of lead and copper were left behind; these were dissolved in nitric acid, the solution evaporated nearly to dryness with a little sulphuric acid, the dissolved oxide of copper filtered and precipitated with potash, and the residuary sulphate of lead weighed after washing and ignition. The

other metallic sulphurets were again precipitated by an acid from the solution in sulphuret of potassium, ignited after being dried with an excess of cyanide of potassium, when the arsenic was volatilized, while the tin and antimony remained, partly in the state of regulus and partly diffused throughout the slag. The residue was dissolved in water, the solution separated from the metals and acidified, and again treated with sulphuretted hydrogen, in order to precipitate those portions of tin and antimony which had been redissolved. From the solution of these sulphurets both metals were precipitated by zinc, and, after drying and weighing, again dissolved in muriatic acid and chlorate of potash, and the antimony precipitated from the solution by a bar of pure tin. The insoluble portion of the mother-ley from 10000 parts water yielded—

	Joseph's spring.	Wenzel spring.	Leopold's spring.
Peroxide of iron	0·2784	0·1835	0·4310
Metals	0·0059	0·0040	0·0090
Relation of the peroxide of iron to the metals	46·7 : 1	47·4 : 1	49·5 : 1

The metals consist of—

Oxide of copper	0·00104	0·00069	0·00156
Oxide of lead	0·00025	0·00016	0·00037
Oxide of antimony	0·00016	0·00010	0·00024
Protoxide of tin	0·00025	0·00017	0·00038
Arsenious acid	0·00600	0·00400	0·00900

1044 bottles of water from the Joseph spring, 516·5 bottles from the Wenzel spring, and 866 from the Leopold spring, contain respectively 1 gr. of arsenious acid.

In the deposit from the spring of the bathing establishment in the Eagle, there was 2·290 metal to 100 parts of peroxide of iron; considering this as arsenic, it would correspond to 3·03 arsenious acid. From the deposit in the spring in the establishment of M. Lade, chemist in Wiesbaden, there was for 100 parts peroxide of iron 1·98 metal = 2·61 arsenious acid; and in the sediment from the Kochbrunnen in Wiesbaden, for 100 parts peroxide of iron, 2·94 metal = 3·88 arsenious acid*.—Liebig's *Annalen*, lxi. p. 192.

Simple Method of Testing Anhydrous Alcohol. *By* M. Casoria.

To ascertain whether alcohol contains water, all that is required is to allow it to stand for some time in a closed vessel with anhy-

* Similar observations have recently been published by Keller respecting the Kissingen water, the sediment from which contains such an abundance of arsenic, that a distinct metallic ring was obtained from only 2 grms. It also contained tin and copper. The chalybeate water of Bruckenau contains a mere trace of arsenic, tin and a tolerable quantity of copper. M. Chatin was not able to detect a trace of arsenic in the water of Passy, which had been examined with a different result by Flandin; but he found some in a spring in the park of Versailles.

drous sulphate of copper. If water be present, it assumes a blue colour, whilst in anhydrous alcohol it remains white.—*Journ. de Chim. Méd.*, 3 ser. ii. p. 466.

PATENT.

Patent granted to C. A. Kurtz, Manchester, *for the Manufacture of a new Colouring Matter, to be used in the Dyeing or in the Printing of Woollen, Cotton, Silk, and other Fabrics.*

This invention consists in the manufacture of a "substantive colouring matter," suitable for dyeing or printing a bronze or brown colour, by subjecting aloes or an extract of logwood to the action of nitric or nitrous acid.

The mode of preparing the colouring matter from aloes is as follows:—Into a boiler or vessel, capable of holding about 100 gallons, the patentee puts 10 gallons of water and 132 lbs. of aloes, and heats the same until the aloes are dissolved; he then adds 80 lbs. of nitric or nitrous acid, in small portions at a time, to prevent the disengagement of such a quantity of nitrous gas as would throw part of the contents out of the boiler. When the whole of the acid has been introduced, and the disengagement of gas has ceased, 10 lbs. of liquid caustic soda or potash of commerce of about 30° are added, to neutralize any undecomposed acid remaining in the mixture, and to facilitate the use of the mixture in dyeing and printing. If the colouring matter is required to be in a dry state, the mixture may be incorporated with 100 lbs. of china clay, and dried in stoves, or by means of a current of air. In preparing the colouring matter from extract of logwood, the materials are used in the manner and proportions above described; the only difference being, that the extract of logwood is substituted for the aloes.

The colouring matter is used in drying, by dissolving a sufficient quantity in water, according to the shade required, and adding as much hydrochloric acid or tartar of commerce as will neutralize the alkali contained in the mixture, and leave the dye-bath slightly acidulated. The article to be dyed is introduced into the bath, which is kept boiling until the desired shade is obtained.

When the colouring matter is to be used in printing, a sufficient quantity is to be dissolved in water, according to the shade required to be produced; this solution is to be thickened with gum, or other common thickening agent; and hydrochloric acid, or tartar of commerce, or any other suitable supersalt is to be added thereto, for the purpose before mentioned. After the fabrics have been printed with the colouring matter, they should be subjected to the ordinary process of steaming, to fix the colour.—Sealed Jan. 27, 1847.

THE CHEMICAL GAZETTE.

No. CXVII.—September 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

An Examination and Analysis of the "Nadelerz," or Needle Ore of Bismuth. By EDWARD J. CHAPMAN, Esq.*

THE "needle ore" occurs in thin prismatic crystals, generally forming more or less radiated groups imbedded in quartz, at Ekatherinenburg in Siberia, the only known locality in which it has been hitherto found. The crystals are too imperfect to admit of measurement; but they appear to belong to the Trimetric or Prismatic system, and to have for the primary form a right rectangular prism, or perhaps more correctly a right rhombic one, in which the angle MM closely approaches a right angle.

The colour of this mineral is dark steel-gray on the fractured surface, but externally the true colour is usually masked by a yellow tarnish. The powder or "streak" is black; the degree of hardness 2·0 to 2·5, or between that of rock-salt and calc-spar; and the specific gravity about 6·1.

Before the blowpipe it fuses instantly and may be almost entirely volatilized, forming a yellow incrustation of the mingled oxides of lead and bismuth on the support. The presence of bismuth and copper may be ascertained by fusion with "microcosmic salt" and a little tin on charcoal in the reducing flame, when the lead, which is clear whilst hot, becomes on cooling of a grayish-black colour with red patches. With carbonate of soda on charcoal in the same flame, it forms an alkaline sulphuret. The lead is best detected by boiling a fragment in nitric acid, filtering, dissolving the residue (sulphate of lead) in caustic potash, diluting the solution, and re-precipitating by sulphuric acid.

This ore was first described by Karsten and analysed by John; and although a considerable period has elapsed since the date of this analysis, yet, probably from the rarity of the mineral, its composition has been examined by but one other chemist, Frick, in Poggendorff's 'Annalen,' xxxi. p. 529.

* Communicated by the Author.

These analyses have given—

1. By John:—

	Per cent.	Atomic relations.	
Sulphur	11·58	0·057	3
Bismuth	43·20	0·032	2
Lead	24·32	0·018	1
Copper	12·10	0·031	2
Nickel	1·58		
Tellurium	1·32		
Gold	0·79		
	94·89		

2. By Frick:—

Sulphur	16·61	0·0826	6
Bismuth	36·45	0·0410	3
Lead	36·05	0·0270	2
Copper	10·59	0·0267	2
	99·70		

The first analysis does not admit of any rational formula; but if we consider the loss, more than 5 per cent., to be sulphur, we may obtain by a little latitude,

$$Cu^2S + PbS + Bi^2S^3, \text{ or } 2\left\{\begin{matrix}Cu^2S\\PbS\end{matrix}\right\} + Bi^2S^3,$$

a formula analogous to that of the kobellite from Ilvena in Sweden, analysed and named by Setterberg, and in which the electro-negative atoms in the base are to the electro-negative atoms in the acid as 2 to 3. The following is its formula:—

$$2\left\{\begin{matrix}FeS\\PbS\end{matrix}\right\} + Bi^2S^3.$$

The second analysis yields also but an inexpressive and unsatisfactory result. The formula, if such it can be termed, obtained from it is—

$Cu^2S + 2PbS + 3BiS$, or otherwise $Cu^2S, BiS + 2(PbS, BiS)$.

I have now to enter into the details of a third analysis, executed lately by myself, on a specimen kindly given to me by Colonel Jackson, F.R.S., who brought it with him from Russia. The ore was accompanied in the quartz by minute tufts of malachite, which, together with the matrix, were carefully removed, by the aid of a microscope, from the substance analysed.

8·38 grs. of the mineral in powder were boiled in strong nitric acid.

A residue of 4·92 grs. of sulphate of lead remained, and 0·26 grs. of sulphur. The 4·92 grs. of sulphate of lead (obtained, it should be stated, after solution of the residue in potash and subsequent reconversion) = 3·36 grs. of lead and 0·52 of sulphur.

Carbonate of ammonia in excess was then added to the clear solution; and after remaining for three hours at a gentle heat, it was filtered from the precipitate, which (after being well-washed with

the same reagent, and the "washings" added to the original solution) was dissolved in acetic acid; and a slip of pure lead being immersed in the solution, the whole was covered up immediately and suffered to stand for four hours. The slip of lead weighed 22·63 grs.

The four hours having elapsed, the lead was taken from the solution, and, after separation of the precipitated bismuth, dried and weighed. It weighed 19·21 grs.; loss, 3·42 grs. On the addition of sulphuric acid, 5·03 grs. of sulphate of lead were obtained, which are equal to 3·435 of lead; and this amount corresponding so nearly with the loss in the metallic precipitant, the whole of the lead present in the mineral may be considered to have been converted into PbO, SO^3 by the first operation.

The bismuth precipitate was washed with cold distilled water (which had been boiled), dissolved in nitric acid, and again thrown down by carbonate of ammonia. The oxide of bismuth weighed 2·60 grs., equivalent to 2·33 grs. of bismuth.

To the original solution (containing carbonate of ammonia) a few drops of ammonia were added, and it was then gently evaporated until the ammoniacal odour was entirely destroyed. Solution of potash was then added, and the whole boiled. The black oxide of copper, well-washed with hot water, ignited, and weighed in a covered crucible, came to 1·31 grs., an amount equal to 1·05 of copper.

Finally, chloride of barium was added to the potash solution, which produced a precipitate of sulphate of baryta weighing 5·72 grs., an amount corresponding to 0·79 of sulphur. The whole of the sulphur present in the mineral was therefore

1·57 grs. (0·52 + 0·26 + 0·79).

The following table exhibits the above analysis and its atomic deductions:—

		Per cent.	Atomic relations.	
Sulphur	1·57	18·78	0·0935	3 or 18
Bismuth	2·33	27·93	0·0315	1 or 6
Lead.....	3·36	40·10	0·0309	1 or 6
Copper.....	1·05	12·53	0·0317	1 or 6
	8·31	99·34		

$$3Cu^2S, Bi^2S^3 + 2(3PbS, Bi^2S^3).$$

This formula is identical with that of the bournonite (from the analyses of H. Rose, Smithson, &c.), substituting only Bi^2S^3 for Sb^2S^3, as below:—

$$\text{Bournonite} = 3Cu^2S, Sb^2S^3 + 2(3PbS, Sb^2S^3).$$

In each ore, the electro-negative atoms in the basic compounds are, to the electro-negative atoms in the acid compounds, as 1 to 1, as expressed in the accompanying general formula:—

$$3\left\{\begin{matrix}Cu^2S\\PbS\end{matrix}\right\} + \left\{\begin{matrix}Sb^2S^3\\Bi^2S^3\end{matrix}\right\}.$$

As the bournonite crystallizes also in the same system as the

needle ore, and indeed affects probably the same primary form within close measurements, the isomorphous relationship of these minerals is sufficiently apparent.

Most English mineralogists give a right rectangular prism for the primary form of the bournonite; but Dufrénoy, in his recent Treatise, vol. iii. p. 18, after an examination of numerous crystals, considers a right rhombic prism in which the angle MM = 93° 40′ to be the correct primary form. The modified rectangular prism in which the bournonite usually occurs is in this light a secondary form, derived from the primary by the replacement of its lateral edges by the planes g' h' in the notation of Hauy.

The specimen of the needle ore which furnished the above analysis, exhibited here and there in the quartz transverse rhombic sections, in which an accustomed eye might easily perceive that the obtuse angle was included between 90° and 100°.

I could not detect in this specimen the presence of tellurium, found by John in the needle ore; it is however perfectly conceivable that, under certain circumstances, a portion of the PbS may be replaced by PbTe.

On the probable Cause of the late Explosion of Gun-Cotton. *By* Robert Oxland, Esq.*

From a series of experiments on the manufacture and use of gun-cotton, and from a careful consideration of the circumstances attending the late terrible accident at Messrs. Hall's manufactory, I have but little doubt that it was occasioned by the means adopted for drying.

I have repeatedly found that gun-cotton is more liable to explode in the course of drying when a certain amount of moisture remains in it, than when more nearly finished.

Why this should be I do not pretend to say; but the consideration of the following fact, which has repeatedly taken place under my own observation, may possibly serve in part to explain the occurrence, and to indicate such an alteration in the mode of drying as may entirely prevent similar accidents for the future. In the course of a series of experiments on the large scale on the commercial value of peat, I have repeatedly had occasion to determine the amount of moisture in the peat which was in use for fuel.

For this purpose, I have weighed out a pound of it, broken to the size of walnuts or thereabout, and placed it in a tin vessel on the top of a still.

The peat thus operated upon usually contained from 20 to 45 per cent. of moisture.

If the peat was not frequently turned over, so as to disperse the warm moist atmosphere formed around it, it would almost invariably take fire, although the temperature indicated by a thermometer placed in the same position was not higher than 160°.

When placed in a much warmer position, but where a current of

* Communicated by the Author.

air could be kept freely passing around it, it would be dried without any risk of combustion and not requiring attention.

As gun-cotton is so much more inflammable than peat, it is not unreasonable to suppose that the same cause operating in the drying both of peat and of gun-cotton, but with the latter substance in a diminished degree, may have been productive of similar results.

Supposing such to be the case, then a similar plan of drying would appear to be necessary. A current of air heated to between 80° and 90° would certainly, under all the circumstances, be the most effective method of drying. I have always found gun-cotton dried in this manner in a better condition than when dried by the stove, and I have supposed it to be more powerful; but of this I cannot speak with certainty, as I have not yet tested it.

Plymouth, Aug. 21, 1847.

Researches on the Bile. *By* Prof. G. J. Mulder.

[Continued from p. 325.]

Putrefied Bile.

The bile from sixteen oxen was set aside in a dish for three weeks in hot weather of the month of July. At the end of this time it was very fœtid; one half was filtered, and the other was left to putrefy for six weeks more. To the first half, neutral acetate of lead was added, which caused a copious granular, but not plastery precipitate; this was much more considerable than in fresh bile. The precipitate was separated by filtration, and the filtrate treated with basic acetate of lead. The precipitate produced by the neutral acetate of lead was diffused in water, and decomposed with acetic acid. A resinous dark brown mass, which speedily became coherent, was formed from it. By kneading with water, it was completely freed from lead.

The resinous mass dissolved entirely in alcohol, forming a clear brown solution, which was perfectly decolorized by animal charcoal. The alcohol was evaporated, and the residue treated with barytic water, by which it was almost entirely dissolved; the fatty acids being at the same time removed: hence little fellinic or cholinic acid was present. A current of carbonic acid was passed through the filtered clear solution, which was then warmed, filtered and evaporated, and the residue dried at 284° F.

The barytic salt remaining yielded a mere trace of sulphuric acid on combustion with nitre and carbonate of potash. Thus the biline, which contains sulphur, was almost entirely decomposed, and the barytic salt was almost entirely free from biline.

When dried at 248° F., it yielded 16·62–16·96, mean 16·79 per cent. of baryta, and on combustion (the nitrogen was determined by volume)—

				Calculated.
Carbon.....	69·72	69·44	100	69·25
Hydrogen	9·54	9·53	84	9·68
Nitrogen	1·35	1·35	1	1·61
Oxygen	19·39	19·68	21	19·46

The substance however is not pure, but appears to be a state of transition from fellinic into fellanic acid in combination with ammonia and a trace of biline; thus

$$(C^{50}\,H^{40}\,O^{10} + NH^3) + (C^{50}\,H^{40}\,O^{10} + BaO).$$

This requires 1·5 per cent. of baryta.

Ammonia was evolved from it when heated with potash; but the whole of the nitrogen could not be expelled by caustic potash; it was not heated with baryta.

This body teaches us that an acid constantly occurs even in putrefying bile, which can be referred to the elements of dyslysine and water, and therefore is analogous in composition to fellinic acid, without however being fellinic acid. Biline thus becomes resolved into a substance which may be expressed by $C^{50}\,H^{36}\,O^6\,n$ aq., ammonia and taurine.

This acid was white, pulverizable, but slightly soluble in water, of an acid reaction, readily soluble in alcohol, and but little so in æther. It was precipitated from the soluble barytic compound by acetic acid as a coherent mass, and became soft by a boiling heat. When washed with water and melted in a water-bath, it formed on cooling a resinous fissured mass. The barytic salt dissolved in water yielded gelatinous precipitates with nitrate of silver and neutral acetate of lead, which were soluble in alcohol. The solution also yielded precipitates with the sulphates of zinc and copper and bichloride of mercury. The substance separated from the barytic salt by acetic acid was readily dissolved by potash, soda, ammonia, lime-water, and the carbonates of potash and ammonia. Hence it contains no cholanic acid; it cannot be fellanic acid, for the bichloride of mercury completely precipitated it from the barytic compound; nor cholic acid, for the cholates of lead, mercury and silver are very readily soluble; nor cholinic acid, because the lead-salt was soluble in alcohol, whilst cholinate of lead is insoluble in alcohol; and cholinate of mercury is also soluble in water. Neither could it be fellinic acid, as its barytic salt is very soluble in water.

I cannot decide with certainty if this is a sixth and new acid; so much is certain, that the quantity of biline which it contained, judging from the amount of sulphur existing in it, cannot have any essential share in the production of its peculiar properties.

From what has been stated, it appears that this acid approximates most, both in properties and composition, to fellanic acid. The nitrogen it contains, which can be almost completely expelled by potash, renders it probable that Gmelin, who described a nitrogenous acid under the name cholic acid, examined a substance which was not completely metamorphosed, and contained traces of biline and ammonia. According to the author's experiments, all the acids which can be obtained from bile are free from nitrogen when not contaminated with biline or taurine, nor containing ammonia; which, as it is a product of the decomposition of the bile, they readily take up and retain in combination. At ordinary temperatures barytic water does not expel the ammonia from acid ammoniacal salts, but forms double salts of ammonia and baryta.

The second half of the putrefying bile, which had been exposed for six weeks longer in summer, and the surface of which was covered with mould, was evaporated to dryness, dissolved in cold water, filtered, and basic acetate of lead added. The granular precipitate was kneaded under water, dissolved in alcohol, filtered, and a current of sulphuretted hydrogen passed through the solution; the sulphuret of lead formed was separated by filtration, and the solution decolorized with charcoal and evaporated. A colourless substance remained. This was exhausted with æther, in which the greater part of it dissolved, leaving a small quantity of a glutinous mass, which still contained a little unaltered biline. The ætherial solution on evaporation left a transparent mass, which when triturated with water formed a white powder; this was collected on a filter, washed and dried. On evaporating the washing-water, a small quantity of the same white powder was deposited on cooling.

This substance was readily soluble in barytic water. On passing carbonic acid through the solution, a little carbonate of baryta was first deposited; the whole mass then became gelatinous, and on continuing the transmission of the gas a small glutinous portion subsided, which was insoluble in a fresh portion of barytic water. The glutinous mass was bilifellinic acid. The white pulverulent substance was not pure, and it was this which originally caused the solution of the glutinous substance. Thus a small quantity of biline had been taken up by the æther, which was not yet decomposed, as also a little fellinic acid.

After the separation of the glutinous mass, the white pulverulent substance was precipitated from the barytic compound by acetic acid, washed with water, dissolved in potash, again precipitated by acetic acid and washed. It formed a white powder, which fused below 212° F., and had the following properties. It was free from nitrogen, sulphur and ash; burnt with flame after previously fusing, and puffing up; when cold, after the fusion, it formed a transparent resinous substance. It was only partly soluble in barytic water; it had therefore undergone some change, for the original acid was very easily soluble in barytic water. When dried at 266° F., it yielded the exact composition of anhydrous fellinic acid; thus—

Carbon	72·17	71·92
Hydrogen	9·86	9·84
Oxygen	17·97	18·24

However, it cannot be fellinic acid, for it was not combined with a base, and must therefore have contained 2HO more in the free state than yielded by the analysis.

The original acid, which had not been treated with potash, and contained a trace of fellinic acid, when not freed from this exhibited the following properties:—It fused below 212° F., burnt with much smoke and flame and without ash. After fusion, it formed a transparent resinous mass, containing neither nitrogen nor sulphur. When heated in water, it became soft without rendering water acid; when placed upon moistened litmus-paper, it reddened it. It was soluble

in alcohol, æther and barytic water. On evaporation, the barytic salt did not crystallize, but formed a gummy mass. The same applies to potash, soda and ammonia. It was readily soluble in carbonate of soda when heated. The solution in ammonia was precipitated by chloride of barium, as stated by Berzelius*. All its alkaline salts froth like soap and water. It was soluble in lime-water, and precipitated from it, as also from the barytic salt, by acetic acid. When the neutral lime-salt was treated with basic acetate of lead, a copious precipitate was formed; the same occurred with neutral acetate of lead, sulphate of copper and of zinc, bichloride of mercury and nitrate of silver. These precipitates do not cohere, but are white and flaky, and are all soluble in alcohol.

Except that the neutral lead-salt is insoluble, all these properties agree with those of Berzelius's fellanic acid; it differs from fellinic, cholinic, cholic and cholanic acids in several points.

In the state in which we had obtained it in our experiments, it made up, in combination with ammonia, nearly the entire mass of the putrefied bile. The fellinic and cholinic acids and the biline have disappeared, and ammonia, taurine and fellanic acid have been formed from the latter.

The composition of this acid, which had not been treated with potash, and was fused and dried at 266° F., was—

		Atoms.	Calculated.
Carbon	70·74	50	71·48
Hydrogen	9·90	40	9·50
Oxygen	19·36	10	19·02

It was dissolved in excess of very weak ammonia, and treated with nitrate of silver. A white flaky silver-salt was formed, which on washing was partly dissolved in water, and hence could not have been neutral. On drying at 230° F., the salt became coloured. It yielded 8·16 per cent. of oxide of silver, and on ultimate analysis—

		Atoms.	Calculated.
Carbon	72·21	150	71·98
Hydrogen.....	9·81	119	9·50
Oxygen.....	17·98	29	18·52

As is shown by the following analyses of the barytic salt, the above salt is neither neutral nor acid, but consists of

$$2(C^{50}\,H^{39}\,O^{9} + HO) + (C^{50}\,H^{39}\,O^{9} + AgO).$$

This requires 8·48 per cent. of oxide of silver.

The same acid was dissolved in barytic water, carbonic acid passed through the solution, which was then heated, filtered and evaporated, and the barytic salt dried at 266° F. It yielded 8·00 per cent. of baryta, and—

		Atoms.	Calculated.
Carbon	71·90	100	72·24
Hydrogen.....	9·63	79	9·48
Oxygen.....	18·47	19	18·28

* Ann. der Chem. und Pharm., vol. xliii. p. 64.

Theory requires 8·4 per cent. of baryta. Thus the formula of the barytic salt is

$$(C^{50}\,H^{39}\,O^{9} + BaO) + (C^{50}\,H^{39}\,O^{9} + HO).$$

The anhydrous fellanic acid will therefore be $C^{50}\,H^{39}\,O^{9}$, and differs from fellinic acid by HO. The results of this analysis agree tolerably with those obtained by Gorup-Besanez (Untersuch. üb. d. Galle, s. 17) with a substance also procured from putrefied bile.

According to Berzelius, fellanic acid is converted into dyslysine by muriatic acid; the substance examined by us possesses this property, and it leaves nothing in solution in the muriatic acid. As the investigation of this dyslysine was important, it was accurately made. After boiling for six hours with muriatic acid (1·13), the fellanic acid had entirely disappeared, having been resolved into fellinic and cholinic acids and dyslysine; these acids were again boiled with muriatic acid. That portion of the residue which was insoluble in alcohol, but soluble in æther, when dried at 266° F. yielded—

		Atoms.	Calculated.
Carbon	76·38	100	76·38
Hydrogen	9·34	74	9·39
Oxygen	14·28	14	14·23

This was dyslysine prepared from fellanic acid.

If the bile be allowed to putrefy still longer, another acid forms the main constituent. The fellanic acid disappears, and is replaced by a crystalline acid; this is Berzelius's cholic acid,

$$C^{100}\,H^{83}\,O^{23} = 2(C^{50}\,H^{36}\,O^{6}) + 11\,aq.$$

It is the same acid as Demarçay obtained on boiling the bile with alkalies, for which Dumas and Pelouze calculate the formula $C^{42}\,H^{36}\,O^{10}$, and Theyer and Schlosser $C^{42}\,H^{38}\,O^{9}$. If carbon be calculated for C 75·12, the results of the formula of the latter chemists agree accurately with those of Gorup-Besanez, as also with the formula $2(C^{50}\,H^{36}\,O^{6}) + 11HO$. In the salts, the acid is probably $C^{50}\,H^{36}\,O^{6} + 5HO$. Whatever may be the equivalent of the above cholic acid, the changes undergone by the biline are certain; it may be completely converted into fellinic and cholinic acids or dyslysine (all of which are $= C^{50}\,H^{36}\,O^{6} + n\,aq$), ammonia and taurine, if cholic acid forms the last product of the putrefaction, or fellanic acid the last but one. On putrefaction, nothing more is formed than one of the acids mentioned, ammonia and taurine. That cholic acid is converted into dyslysine by muriatic acid has been shown by Berzelius. We thus see the connexion existing between the composition of the two and all the compounds which have been described.

On briefly summing up the results which have been detailed, we find that the following substances are formed from the bile by putrefaction and the action of muriatic acid,—taurine, ammonia and $C^{50}\,H^{36}\,O^{6} + n\,aq$. The latter forms different substances by taking up or parting with the elements of water.

Dyslysine insoluble in æther.....	$C^{50}\,H^{36}\,O^{6}$ (?)
Dyslysine insoluble in alcohol	$C^{50}\,H^{36}\,O^{6} + \frac{1}{2}HO$
Dyslysine soluble in boiling alcohol..	$C^{50}\,H^{36}\,O^{6} + HO$
Cholinic acid	$C^{50}\,H^{36}\,O^{6} + 2HO$
Fellanic acid	$C^{50}\,H^{36}\,O^{6} + 3HO$
Fellinic acid	$C^{50}\,H^{36}\,O^{6} + 4HO$
Cholic acid	$C^{50}\,H^{36}\,O^{6} + 5HO$(?).

Cholanic acid is probably isomeric with one of the above acids. It belongs to the above series, but its composition is unknown.

These substances are the principal products of the decomposition of the biline, and will now enable us to form further conclusions as to its composition; for if, on its decomposition, we always have $C^{50}\,H^{36}\,O^{6} + n$ aq, ammonia and taurine only formed, biline must contain the elements of these matters.

This composition of the biline also explains its relations. As bile is kept, at first fellinic and cholinic acids increase and the biline diminishes, and ammonia becomes combined with the acids; at last the taurine increases.

Further, as the bile gets still older, the biline continues to diminish, and in the place of the fellinic and cholinic acids we have fellanic and cholanic acids. Finally, the biline is entirely decomposed; the fellinic acid has then nearly disappeared, as also fellanic and cholanic acids; and, at last, cholic acid takes the place of all the others. All these acids are converted by muriatic acid into dyslysine, and the latter by potash in alcohol is again reconverted into cholinic and fellinic acids. There is no question then that the one substance yields the material for all the rest.

If the interpretation of the analyses is correct, dyslysine, fellinic, cholinic, fellanic, cholanic and cholic acids are bodies which are allied to each other, as starch, gum, vegetable mucus, cane-, grape- and milk-sugar and glucose.

[To be continued.]

On the Composition of the Air in Places in which numerous Persons or Animals breathe. *By* M. Lassaigne.

In the ventilation of rooms, &c. it is frequently supposed that the lower layers of the air are those which are principally spoiled by respiration. In 1842, Leblanc showed that, at the close of the performance in one of the Paris opera houses, the upper layers of air contained 0·0043 carbonic acid; the lower ones, on the contrary, only 0·0023. It may be objected to this experiment, that in this case the greater portion of the carbonic acid arose from the illumination, and that moreover no very accurate result could be obtained on account of the nature of the locality. The author made his experiment in a small lecture-room in which 55 persons had breathed for $1\frac{1}{2}$ hour, and in which, as far as it was possible, all communication with the external atmosphere was cut off. The capacity of the lecture-room amounted, deductions made for furniture, to 280000

litres. If we subtract 3520 litres as the average volume of 55 persons, there remains for the air contained in the lecture-room 276480 litres. Two samples of the air were examined (half-past 12 o'clock in the morning), one of which was collected near the ceiling, the other near the ground. The air, confined over mercury, was first passed through caustic potash to remove the carbonic acid, and the oxygen then determined by means of phosphorus. The following are the results:—

	Air from the ceiling.	Air from the ground.
Oxygen.....	19·80	20·10
Nitrogen	79·58	79·35
Carbonic acid	0·62	0·55
	100·00 vols. at 30 Bar. and 66° F.	

We find, therefore, likewise in this case the quantity of the carbonic acid contained in the upper strata somewhat greater than in the lower, if indeed the difference must not be ascribed to an error of observation, for it is generally established that the carbonic acid remains pretty much alike in the lower and in the upper strata. If we admit that there is 0·0005 carbonic acid contained in ordinary air, and that the air examined contained 0·0058, consequently 11 times more carbonic acid, we obtain for the lecture-room 1603·78 litres, and after deducting the usual amount of carbonic acid contained in the air, 1465·6 litres; consequently for each of the 55 persons that breathed in the lecture-room 26·64 litres for $1\frac{1}{2}$ hour, and 17·76 litres for 1 hour = 0·281 of the volume of the body = 32·85 grm. carbonic acid at 32° F. and 29·8 barometric pressure, = 8·96 grms. carbon. In a second experiment, the air near the ground of the lecture-room contained 0·0043, that from the ceiling 0·0049. The smaller quantity of carbonic acid found in this case appears to have arisen from a slight change of air having occurred.

The author obtained similar results in examining the atmosphere from a very confined stable. The door and window of the stable were most carefully stopped up during the experiment (45 minutes;) and upon this a sample of the air taken from near the ceiling, the other from near the ground. They yielded on examination—

	Air from the ceiling.	Air from the ground.
Nitrogen	79·47	80·10
Oxygen.....	20·01	19·35
Carbonic acid	0·52	0·55

The quantity of the carbonic acid contained in the confined stable amounted to 78·50 cubic metres = 78500 litres at 84°; and after deduction of the volume of the two horses in it (together 1332 litres) 77168 litres. The quantity of the carbonic acid amounted to 401·27 litres, and after deducting the previous amount of carbonic acid (= 38·58 litres), is 362·69 litres. The horses breathed 483·58 litres in 1 hour; each horse therefore 241·79 litres carbonic acid at 84° F. and 30 Bar. = 219·72 litres carbonic acid

at 32° F. and 29·8 Bar., or 0·328 of the volume of the animal. The volume of carbonic acid expired by a man in 1 hour is to that expired by a horse as 17·16 : 219·72, and calculated for equal volumes of body as 0·281 : 0·328. While a man burns in 1 hour 8·96 grms. of carbon, a horse consumes 110·21 grms.—*Journ. de Chim. Méd.*, ii. pp. 477 and 751.

On Harmaline. By J. Fritzsche.

The seeds of *Peganum Harmala*, which grows in great abundance in the steppes of Southern Russia, are used for the preparation of a very beautiful red colouring substance, which does not pre-exist in them, but is formed from an alkaloid—harmaline, respecting which Göbel has already published a brief notice. Besides the harmaline, however, these seeds contain another alkaloid, harmine, which will be described on some other occasion. Both these alkaloids are contained in the shell, whilst the kernel yields but mere traces; they are best obtained by exhausting the pounded seed in an ordinary displacement apparatus with water, to which acetic or sulphuric acid has been added. A brownish-yellow solution is obtained, which contains, besides the salts of the alkaloids, some other substances, from which they are freed by precipitation with chloride of sodium. The quantity of salt requisite to precipitate the alkaloid salts depends on the acidity of the liquid; very acid liquids must be perfectly saturated with salt. The muriates thus obtained are still more or less coloured; they are collected on a filter, and washed with a solution of chloride of sodium until all adherent mother-ley is removed; they are then dissolved by pouring cold water upon them, when a portion of the colouring substance remains undissolved on the filter, and a dark yellow or a brownish solution is obtained, which is decolorized as much as possible by animal charcoal. The harmine is now first precipitated from the liquid by caustic ammonia, and subsequently the harmaline. For this purpose, a solution of caustic ammonia is added in drops to the liquid, heated to between 122° and 140°, with constant stirring, until a precipitate begins to appear, the amount of which generally increases rapidly without any further addition of ammonia, but merely by agitation. Harmine forms acicular, harmaline laminar crystals; so that it is very easy to ascertain by the microscope whether pure harmine has been precipitated or not. If any harmaline is present, the precipitate must be dissolved in a little acid, and again submitted to the above treatment. The two alkaloids may also be separated by dissolving them in acetic or muriatic acid in alcohol, and adding to the hot solution excess of ammonia. When harmine is present, it very soon separates in the form of long prismatic crystals; harmaline, on the contrary, is very slowly deposited; so that when the separation of the harmine has resulted, the liquid is filtered still hot, and the harmaline precipitated with an excess of ammonia. Instead of employing chloride of sodium to precipitate the alkaloid salts, nitrate of soda may be used; but as nitric acid very readily decomposes the alka-

loids, care must be taken to avoid the presence of free sulphuric acid when nitrate of soda is applied. On decolorizing with charcoal, the liquid should be as neutral as possible; solutions of the acetates must not be heated with charcoal, because a considerable amount of harmine is precipitated. The quantity of the alkaloids obtained amounted to about 4 per cent., of which the harmaline forms about two-thirds and the harmine one-third. This relation is, however, not constant.

Harmaline.—In the pure state it is quite colourless, but it is usually obtained of a somewhat brownish colour. To obtain it perfectly pure, it is diffused in water, acetic acid added until the greater portion is dissolved; the filtered solution diluted, and precipitated with nitrate of soda, chloride of sodium or muriatic acid, upon which it is again filtered, and the salt, after being washed with a solution of the precipitant employed, dissolved off the filter with lukewarm water. The solution is digested with animal charcoal till it possesses a light yellow colour; it is then precipitated, whilst still hot, by an excess of caustic potash. If the precipitate is not perfectly white, the same operation must be partially or wholly repeated; and even then the preparation usually acquires a brownish tint on filtration and washing, especially when ammonia has been employed instead of potash to precipitate it. This colouring is undoubtedly owing to the influence of the oxygen of the atmosphere. The harmaline thus obtained forms broad laminar and scaly crystals of pearly lustre, which are of larger size the more slowly the precipitating agent was added. To obtain it in larger crystals, it should be again dissolved in acetic acid, thrown down by nitrate of soda, the precipitate dissolved in cold water, and the boiling solution precipitated by potash. After washing the precipitate with water which has been boiled, it is transferred while still moist into a flask, the aperture of which is closed hermetically by a cork furnished with a conducting tube, the one arm of which, more than 30 inches long, terminates under mercury. Hot absolute alcohol is poured over the precipitate, the flask closed and heated to boiling until all the air has been expelled by the vapours of alcohol, when the lamp is removed, and the liquid left to crystallize in the apparatus closed by mercury. In this manner perfectly colourless crystals are obtained, which is barely possible by the other methods.

Harmaline is sparingly soluble in water; but on its precipitation from the aqueous saline solutions, a tolerable quantity is left in the liquid; it is nearly tasteless, while its salts are very bitter. When ammonia is added to an aqueous solution of a salt of harmaline, a turbidness results at first from the alkaloid separating in small oily drops; these drops soon disappear, larger crystals being formed, which however are slow in making their appearance in those solutions containing colouring substance. When concentrated solutions are precipitated in the cold by a large quantity of ammonia, the drops aggregate to a more or less soft mass; the solutions of harmaline must therefore not be precipitated cold, but hot, and the ammonia added gradually. Harmaline is very sparingly soluble in cold

alcohol, so that it may be washed with it; boiling alcohol dissolves it readily, and it separates from the solution in small crystals, which are generally somewhat coloured; it is scarcely soluble in æther, and is precipitated by it in a crystalline state from a concentrated alcoholic solution. Harmaline dissolves slightly in boiling naphtha, from which it separates in crystals on cooling, without the crystals becoming coloured by long boiling. Recently rectified oil of turpentine and oil of lemons likewise dissolve small quantities of harmaline, but are quickly coloured by it if not recently rectified. Harmaline expels ammonia from its salts on the application of heat; and when impure harmaline is boiled with a solution of chloride of ammonium, a portion of the colouring substance is retained, while the muriate of harmaline crystallizes from the liquid. Even the purest harmaline forms yellow solutions and sulphur-coloured salts with acids. On analysis, the author obtained similar results to those of Will and Varrentrapp; but he prefers the formula $C^{27}H^{14}N^{2}O^{2}$.

Carbon	73·92	73·42	73·64	73·70	27	= 2028·24	73·67
Hydrogen ..	6·56	6·54	6·55	6·63	14	174·72	6·35
Nitrogen	12·33	..	..	..	2	350·12	12·72
Oxygen	..	..	..	..	2	200·00	7·26
						2752·08	

The slight excess of water is probably owing to the formation of a small quantity of nitric acid during the combustion in Hess's apparatus, but not to the presence of a larger amount of hydrogen in the harmaline. The author regards harmaline as a conjunct ammonia, and places it in the class of alkaloids the conjuncts of which contain nitrogen.

Hydrochlorate of Harmaline.—This salt is most readily obtained by precipitating the acetate or sulphate of harmaline with chloride of sodium, in a solution of which it is sparingly soluble; but it is still more advantageous to use hydrochloric acid to precipitate the acetate of harmaline, in which the hydrochlorate of harmaline is nearly insoluble. If the salt, after washing it with hydrochloric acid, does not possess a light yellow colour, it may be purified by dissolving it in cold water, and again precipitating it with dilute hydrochloric acid. The hydrochlorate of harmaline forms long, slender, prismatic crystals of a yellow colour, which contain 4 equivs. water, part of which however it readily loses. It dissolves pretty easily in alcohol and water. On analysis, it yielded—

Carbon	63·05	63·21	27 =	2028·24	63·208
Hydrogen	5·77	5·86	15	187·20	5·834
Nitrogen.....	..	..	2	350·12	10·911
Oxygen	..	..	2	200·00	6·233
Chlorine.....	..	..	1	443·28	13·814

To ascertain the amount of hydrochloric acid, the salt was first precipitated with ammonia, and the wash-water treated with nitrate of silver; the following results were obtained:—

Harmaline.....	83·91	84·07	82·59	83·60	2753·08	85·797
Hydrochloric acid	14·04	14·24	14·11	14·06	455·76	14·203
					3208·84	

The water in the fresh crystals amounts to 12·60 per cent., or 4 equivs.

The hydrochlorate of harmaline forms with chloride of platinum a double salt, which served the author to determine the atomic weight of harmaline. A dilute aqueous solution of the hydrochlorate, acidified with hydrochloric acid, is mixed in the cold with a dilute solution of platinum, and the bright yellow precipitate left in the liquid until it has become perfectly crystalline, when it is collected on a filter, washed and dried. It forms a light crystalline powder, and yielded upon analysis—

Carbon	37·56	37·69	..	27	=2028·24	38·071
Hydrogen	3·51	3·58	..	15	187·20	3·514
Nitrogen	..	..	..	2	350·12	6·572
Oxygen	..	..	..	2	200·00	3·754
Chlorine.....	..	..	..	3	1329·84	24·962
Platinum	23·39	23·45	23·19	1	1232·08	23·127

The hydrochlorate of harmaline forms with the perchloride of mercury a nearly insoluble double salt, which separates on cooling in a crystalline state on mixing hot solutions. Cold solutions yield dense flocculent precipitates, which likewise exhibit a crystalline structure under the microscope.

Hydrobromate of Harmaline is obtained in the same manner as the hydrochlorate, by adding a solution of bromide of sodium to one of acetate of harmaline, when the salt separates in yellow crystals.

Hydriodate of Harmaline is obtained in the same manner, substituting iodide of potassium for the bromide; it forms a crystalline precipitate, which may be washed with water without much loss.

Hydrocyanate of Harmaline does not appear to exist in an isolated state, for although a peculiar body, containing the elements of the hydrocyanate of harmaline, is formed on mixing harmaline with hydrocyanic acid, or solutions of salts of harmaline with cyanide of potassium, yet it cannot be regarded as the hydrocyanate. In combination with the proto- and percyanide of iron it can exist, and forms with them constant double salts of sparing solubility. The protocyanide is obtained best by adding an excess of the ferrocyanide of potassium to a dilute boiling solution of the muriate of harmaline; a portion of the new compound immediately falls in the form of a brick-red crystalline powder, while the remainder separates from the motherley on cooling. The percyanide is obtained by mixing a dilute boiling solution of harmaline with a solution of ferridcyanide of potassium, when it gradually separates on cooling in long prismatic crystals of a dark greenish-brown colour. Cold solutions when mixed become turbid from the separation of oily drops, which gradually change into crystals; the hot solution likewise becomes turbid when rapidly cooled. Both double salts are at first dissolved by

concentrated muriatic acid, and subsequently unaltered muriate of harmaline separates in a crystalline form.

Hydrosulphocyanate of Harmaline is a sparingly soluble salt, which separates as a bright yellow crystalline precipitate on mixing together dilute solutions of muriate of harmaline and sulphocyanide of potassium. It may be obtained by recrystallization in slender compressed silky needles.

Hydrosulphate of Harmaline is formed when a concentrated solution of acetate of harmaline is added to a concentrated solution of sulphuret of ammonium, which is perfectly saturated with sulphuretted hydrogen, when it separates in minute prismatic crystals. It may be preserved unaltered in the mother-ley in closed vessels, but is very rapidly decomposed in the air; and under the microscope the crystals are seen to become opake and converted into minute adherent crystals of harmaline. If the mother-ley be filtered from the salt, and this dissolved in water, some harmaline remains on the filter; and if the solution be again mixed with the mother-ley, only a partial separation of the salt takes place, or if too much diluted, none at all; but after some time crystalline harmaline is deposited. Owing to this behaviour, the constitution of the salt could not be more accurately determined.

Sulphate of Harmaline.—When harmaline is digested with an insufficient quantity of sulphuric acid to dissolve the whole, a yellow solution of the neutral salt is obtained, which on evaporation at a gentle heat dries to a transparent yellow varnish, but on slow evaporation over sulphuric acid may be obtained as a light yellow radiately-crystalline mass. If an excess of sulphuric acid be added to a concentrated solution of the neutral salt, an acicular acid salt separates after some time, which is readily soluble in water.

Sulphite of Harmaline is obtained by dissolving harmaline in aqueous sulphurous acid, and dries to a yellow varnish.

Nitrate of Harmaline forms light acicular crystals, and may be prepared either by precipitating a dilute solution of acetate of harmaline by dilute nitric acid, or by nitrate of ammonia. It is very sparingly soluble in cold water, especially in the presence of nitric acid; so that it may be precipitated almost entirely from the solution by nitric acid.

Phosphate of Harmaline.—When pulverulent harmaline is boiled with moderately-strong phosphoric acid, this salt separates in acicular crystals on evaporating the solution. An addition of phosphoric acid precipitates an acid salt of similar form in great abundance.

Carbonate of Harmaline.—The neutral carbonated alkalies either yield no precipitates with salts of harmaline, or they separate pure harmaline. When, on the contrary, a solution of acetate of harmaline is mixed with a concentrated solution of bicarbonate of potash, a precipitate soon forms of bicarbonate of harmaline in delicate acicular crystals. If this is quickly washed with very cold water, then carefully pressed between blotting-paper and dried in the air, it is possible to obtain it undecomposed; but if it is left on the filter after the washing, it soon decomposes, and leaves pure

harmaline. The solution of the salt likewise decomposes readily on exposure to the air. The author found nearly 13 per cent. of carbonic acid and 78 per cent. harmaline in the dry salt, which proportion shows that the salt must be considered as a bicarbonate.

Oxalate of Harmaline.—Powdered harmaline, heated to boiling with a little water, and mixed with a solution of oxalic acid not sufficient to dissolve the whole, yields a liquid which on cooling deposits acicular crystals of the neutral salt. An excess of oxalic acid produces in the solution a considerable precipitate of an acid salt.

Acetate of Harmaline.—A solution of harmaline in acetic acid yields, on evaporation at the ordinary temperature, a syrupy liquid, which becomes crystalline on further evaporation without losing its solubility in water. When evaporated over the fire, a portion of the harmaline separates in a crystalline form, owing to the escape of some acetic acid, and is left behind on redissolving the salt.

Chromate of Harmaline. I. *Neutral Salt.*—Dilute solutions of the neutral chromate of potash and harmaline remain clear when mixed in the cold; on the application of heat, crystalline harmaline separates, which also takes place in the cold when more chromate is added to the mixed solutions. If a solution of acetate of harmaline is gradually added with constant agitation to a cold saturated solution of neutral chromate of potash, harmaline first separates; but if it be filtered, and a still further quantity of concentrated solution of harmaline added to it, a bright yellow crystalline salt is soon deposited, which is the neutral chromate. If some solid neutral chromate of potash be placed in a concentrated solution of acetate of harmaline, the liquid becomes turbid for a moment until nearly saturated with the chromate, when on the further addition a thick mass separates on the sides of the vessel, so that it may be separated by decantation from the mother-ley. If this mass is first rinsed with a little water, and more water is then poured upon it, a portion redissolves, and a clear, deep yellow solution is obtained on filtration, which after a time deposits neutral chromate of potash mixed with crystals of harmaline. By adding this solution to the mother-ley, the author obtained pure neutral chromate of harmaline, which, after it has once acquired the crystalline form, dissolves with far greater difficulty in water. This salt can therefore be obtained in two forms; the liquid one passes gradually into the solid one without solution being necessary. On the contrary, the liquids must not be diluted, as they then deposit harmaline.

II. *Acid Salt.*—Dilute acid solutions of harmaline immediately yield, with solutions of chromic acid or with bichromate of potash, beautiful orange-coloured precipitates, which at first separate in the form of minute drops, but soon form into groups of crystals. Salts of harmaline are entirely precipitated by an excess of chromic acid. The compound obtained is the bichromate of harmaline, of the same composition as the potash salt. It dissolves in boiling alcohol without alteration, and separates again on cooling in crystals, from which the harmaline may again be removed by dilute caustic potash. On drying, it may be heated without any change up to 248°; but then it is quickly converted into a dark-coloured body containing chro-

mium; so that the sides of the vessel are quickly coated with a dark-coloured substance containing chromium, and a partially volatile substance, harmine.—*Bulletin de l'Acad. de St. Pétersb.*, vi. p. 49.

On the Detection of Bicarbonate of Lime in Spring Water. *By* A. Dupasquier.

Some time ago the author recommended the use of tincture of logwood to detect bicarbonate of lime in spring water, which it colours violet; but since this reaction may likewise be produced by the presence of other alkaline bicarbonates, the author suggests two other means, by the comparative use of which it may be ascertained whether the water contains bicarbonate of lime or another alkali. The author takes two glasses filled with water, and adds to the one a few drops of a neutral solution of *sulphate of copper*, and to the second some *chloride of calcium*. If the water contain only bicarbonate of lime, a precipitate of carbonate of copper is formed, from the quantity of which the amount of bicarbonate of lime present may be estimated. No precipitate is formed by the chloride of calcium; but if carbonate of potash or soda is present, a precipitate falls on the addition of chloride of calcium. If the quantity of bicarbonate of potash or soda is very small compared to the amount of lime salt present, the precipitate by chloride of calcium may be prevented by the free carbonic acid of the water; on which account from 10 to 15 grms. of the water is heated in a loosely-closed vessel, but not to boiling, so as to expel the excess of carbonic acid without decomposing the bicarbonate of lime. Now if the latter is accompanied with some bicarbonate of potash or soda, the water is rendered turbid; but if bicarbonate of lime is alone present, it will remain clear. In general the bicarbonate of lime in spring water is accompanied by traces of bicarbonate of magnesia, which behave like the bicarbonate of lime towards the above reagents, but is of no consequence with respect to the use of the water for dyeing or drinking.—*Comptes Rendus*, xxiv. p. 808.

How to distinguish Stains of Blood from other Stains.

Persoz found that blood-stains are blackened by hypochlorous acid, while most colouring substances are bleached by it. Brame adds, that the hypochlorous acid should be free from the perchloride of mercury, as it is easily obtained by Williamson's * method, or by agitating fresh chlorine-water with peroxide of mercury. The same author advises removing the stains with faintly-alkaline water, and then performing the experiment in a glass tube. The solution then appears, at a certain degree of concentration, red by reflected light and greenish by transmitted light. M. Buchner states, that the presence of mercury does not appear to interfere in the least with the reaction of the acid, and that the blood-stains instantly become brown, but not black. Chloride of lime or chloride of soda and an addition of muriatic acid may also be employed.—Liebig's *Annalen*, lx. p. 377.

* Phil. Mag., vol. xxvi. p. 231.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the most advantageous Method of extracting Iodine from dilute Solutions. By J. Persoz.

Now that iodine is so extensively used in medicine, and that its price is constantly on the increase, the want is felt more than ever of extracting it with the greatest œconomy both from the waters which contain it naturally, as from those of baths into the composition of which it enters, and even from the urine of the patients submitted to a course of iodine. Soubeiran, finding the process previously followed for the extraction of iodine from the mother-waters of the Varech sodas too tedious and expensive, proposed to precipitate this body by sulphate of copper, to which a certain quantity of iron filings was added, with a view to reduce the periodide of copper to the state of protiodide. Subsequently the protosulphate of iron was substituted for the iron filings.

The irregularity of the results obtained by both these processes must have struck every one who has tried them; it is therefore not surprising that a more certain method has been proposed as a substitute. MM. Labiche and Chantrel have described one which is based upon the insolubility of the iodide of starch, but which in practice presents a difficulty which these gentlemen seem to have overlooked. In fact, iodine combines with starch only when it is in a free state; it is consequently requisite to liberate it from its combinations by means of chlorine, and this presents an insurmountable difficulty.

Having been called upon to examine this question, I found, in the first place, that the protacetate of iron, substituted for the protosulphate, produces a more rapid reduction; but as it is impossible to reckon upon a regular precipitation of the protiodide of copper, owing to the influence which the respective proportions of the solutions employed exert, I had recourse to sulphurous acid, a powerful reducing agent, and whose action upon the peroxide of copper, which it reduces partially to the state of protoxide, was pointed out by M. Chevreul. A few words will suffice to render this kind of reaction intelligible. If 1 grm. of persulphate of copper be dissolved in 150 centigrms. of water, and to this solution 1 grm. of sulphite of soda be added, the liquid acquires a green colour, and becomes turbid. As the formation of a precipitate should be avoided, and at the same time the liquid decolorized, the requisite quantity of sulphurous acid to obtain this double result is added; on letting fall a drop of a solution of iodide of potassium into it, it immediately becomes opalescent, the turbidness goes on increasing, and in the course of an hour a white, slightly-pinkish precipitate of the protiodide of copper is formed, which is readily collected by boiling the liquid for a few minutes, and then decanting.

Accordingly, in treating iodurettedwaters, sulphurous gas should be passed into them until they exhale a faint odour, in order to convert

all the iodine which may exist in the state of iodate into iodurctted hydrogen; then to prevent the formation of the precipitate from the mutual action of the sulphite of soda and the persulphate of copper; and lastly, to cause the reduction of the peroxide of copper. For this purpose, therefore, there is successively dissolved in the liquid under treatment 1 part of persulphate of copper and 1 part of bisulphite of soda, calculating approximatively the amount of the first for the quantity of iodine supposed in solution, upon the fact that about 3 parts of the persulphate of copper are required for 1 part of the iodide of potassium or sodium. The liquid is then left to itself or boiled, according to whether the precipitate is desired immediately or after a few hours. On letting the precipitate form in conical vessels, it is easy to collect it into a small volume; in every case it is brought upon a filter, washed, dried, and the iodine extracted by one of the known processes. Calcining the protiodide of copper, previously mixed with 2 equivs. of peroxide of manganese, may be successfully employed. The reaction above described is so readily produced, that we have no doubt that in future all iodurctted waters, even the weakest, will be treated by this process; and that it will likewise be successfully employed for the analyses of mineral waters containing bromine and iodine.—*Journ. de Pharm. et de Chim.*, Aug. 1847.

New Method of treating Platinum Ores. By J. Hess.

I have frequently observed that the expense of treating platinum ores is principally owing to their being acted upon with great difficulty by *aqua regia*, of which they require from 8 to 10 times their weight; this is avoided by the following process:—The ore is fused with from 2 to 3 times its weight of zinc; when this has been done well, a perfectly homogeneous, very brittle mass is obtained, which is reduced to powder and passed through a sieve. The alloy is now treated with dilute sulphuric acid, which is added in small portions, and renewed when the liquid is saturated; subsequently an acid of $SO^3 + 6HO$ is used, and its action assisted by heat. When nothing further dissolves, the residue is washed with water. The sulphuric acid removes the zinc and the greater portion of the iron; the solution is not rendered turbid by sulphuretted hydrogen. The residue, which is in a very fine state of comminution, is now treated with nitric acid, which removes iron, copper, lead, and sometimes palladium, from it. The iron proceeds from the zinc employed.

The residue, which is at present freed from those metals which render the working difficult, is now treated as usual with *aqua regia*, in which it dissolves with great readiness on account of its fine division. It may readily be seen, that when the acid contains much muriatic acid a large quantity of osmium-iridium is dissolved; an excess of hydrochloric acid should consequently be avoided.—*Journ. für Prakt. Chem.*, June 1847.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of Legumine. *By* Mr. Henry M. Noad*.

Mulder states, in his 'Chemistry of Animal and Vegetable Physiology,' page 297, that the composition of the nitrogenous constituent of the seed of peas, beans, lentils, and other leguminous vegetables, called by Liebig *vegetable caseine*, is still unknown. The experiments of Jones† give it the following composition:

Carbon	55·05
Hydrogen	7·59
Nitrogen	15·89
Oxygen	21·17

Those of Dumas and Cahours‡, on the other hand, lead to the following numbers:—

	Dried at 284° F. *in vacuo*.
Carbon	50·46
Hydrogen	6·65
Nitrogen	18·19
Oxygen	24·70

Rochleder analysed proteine from legumine§, and obtained the following results:—

	Dried at 266° F.
Carbon	54·49
Hydrogen	7·40
Nitrogen	14·78
Oxygen	23·33

But Mulder remarks, that the substance analysed by Rochleder had been acted on by caustic potash; it was therefore no longer *legumine*, having been changed into proteine and mixed with another substance. More recently, Rüling‖ has published some new analyses of the different animal and vegetable nitrogenous principles;

* Communicated by the Author.
† Ann. der Chem. und Pharm., 1841, vol. xxxix. p. 129, and vol. xl. p. 65.
‡ Ann. de Chim. et de Phys., 1842, vol. vi. p. 426.
§ Ann. der Chem. und Pharm., vol. xlvi. p. 162.
‖ Chem. Gaz., vol. iv. p. 362.

his results do not differ from those generally received, with the exception of *legumine*, for which he gives the following composition :—

	Dried at 212° F.
Carbon	50·59
Hydrogen	6·83
Nitrogen	16·54
Oxygen	25·57
Sulphur	0·47

In this determination the numbers for carbon and hydrogen agree pretty nearly with those of Dumas and Cahours; the nitrogen however is nearly 2 per cent. less, and agrees better with the analysis of Jones. In this uncertain state of the subject, I thought that some fresh analyses would be useful; the composition of this substance is indeed a matter of no little scientific interest; for if the numbers given by Dumas and Cahours be received as correct, then legumine cannot belong to the *proteine* class of compounds, but would be more nearly allied to the gelatinous group; but if this be really the case, then it must follow, either that beans, peas, and other leguminous plants, are unfit for the food of animals, or that the deductions from the results of recent chemical investigations, viz. that the food of graminivorous animals must be identical in composition with the chief constituents of the blood, *fibrine* and *albumen*, are incorrect. Now to assert that beans and peas are not as articles of food highly nutritious would be against all experience; and a farmer would very properly laugh at a chemist, and hold his science in utter contempt, were he to attempt gravely to convince him that the extra allowance of beans which he serves out to his team, when they are about to undergo an unusually hard day's work, is so much waste of money, for that, as the nitrogenous principle of beans is not identical in composition with animal fibrine, so this food cannot help to keep up the vital process in the animal.

The following comparison of the analysis of legumine by Dumas and Cahours with that of gelatine from isinglass by Mulder*, will show how nearly allied in composition these substances are according to the analyses of the French chemists; indeed the two analyses do not differ from each other more than two analyses of the same substance frequently do :—

	Legumine, according to Dumas and Cahours.	Gelatine from isinglass, according to Mulder.
Carbon	50·46	50·76
Hydrogen	6·65	6·48
Nitrogen	18·19	18·31
Oxygen	24·70	24·29

The legumine employed in the following analyses was prepared from peas and beans. I did not think it necessary to make any determinations of the amount of sulphur, there being no reason to doubt the accuracy of Rüling in this particular in the experiments

* Chemistry of Animal and Vegetable Physiology, p. 322.

above alluded to. With regard to the methods of determining the amount of this element in organic substances:—The process of Heintz, described in page 315 of the present volume, does not seem to me to offer sufficient advantages over the method of Weidenbusch (p. 215), or the older method by burning with nitre and caustic potash, to warrant the far greater trouble and complication of the process. The method of Weidenbusch is, no doubt, susceptible of great accuracy; I doubt however whether, on the whole, it will be found more convenient than fusing with caustic potash and nitre; the only objection to which is the difficulty of procuring potash perfectly free from sulphur, a difficulty I may observe now nearly removed.

Preparation of Legumine from Peas.

Ground peas were covered with distilled water, and allowed to remain for twenty-four hours, being frequently stirred; the infusion, after the deposition of the starch, was filtered through linen, and the legumine precipitated by sulphuric acid; it was then thrown on a filter, washed well with distilled water, redissolved in ammonia, filtered, reprecipitated by acetic acid, and again well washed, it was afterwards digested twice with alcohol and once with æther, and dried in the water-bath at 212°.

It was burned in the usual way with chromate of lead.

I. 0·3965 grm. gave 0·767 grm. carbonic acid and 0·2815 grm. water.

II. 0·3650 grm. gave 0·7065 grm. carbonic acid and 0·2595 grm. water.

III. 0·538 grm., dried for several hours at from 270° to 300° in a Rammelsberg's air-bath, gave 1·074 grm. carbonic acid and 0·365 grm. water.

IV. 0·3615 grm., burned with soda-lime according to the method of Will and Varrentrap for the determination of nitrogen, gave 0·918 grm. of the double chloride of platinum and ammonium. These numbers correspond with the following per-centages:—

	I. Dried at 212°.	II. Dried at 212°.	III. Dried at 300°.	IV.
Carbon	52·76	52·79	54·40	
Hydrogen.....	7·88	7·89	7·53	
Nitrogen	..	..	..	15·94

Legumine from Beans.

Haricot beans were soaked in water for twenty-four hours, then reduced to a pulp and infused in distilled water with frequent stirring; the clear infusion was treated precisely as in the preceding.

I. 0·507 grm., dried at 212° and burned with chromate of lead, gave 0·996 grm. carbonic acid and 0·355 grm. water.

II. 0·294 grm., dried at from 270° to 300°, gave 0·5935 grm. carbonic acid and 0·201 water.

III. 0·295 grm. gave 0·716 grm. of double chloride of platinum and ammonium.

These numbers correspond with the following per-centages:—

	I. Dried at 212°.	II. Dried at 300°.	III.
Carbon	53·57	55·05	
Hydrogen	7·79	7·59	
Nitrogen	..	..	15·26

The last carbon and hydrogen numbers obtained from the analysis of legumine from haricot beans dried at 300° agree, it will be perceived, exactly with those of Jones; the nitrogen is about $\frac{1}{2}$ per cent. lower; the nitrogen obtained from the legumine of peas agrees almost exactly with that of Jones; and the whole results taken together prove beyond doubt that legumine *is* a proteine compound, identical in composition with fibrine and albumen, and that the analyses of Dumas and Cahours and Rüling are founded on error, having probably been made with impure substances.

1 New Milman Street, Russell Square,
September 8, 1847.

On an Impurity in Commercial Bromine. *By* M. Poselger.

On distilling some commercial bromine, the author found that its boiling-point rose from 122° to 248°, and that the colour of the residuary bromine became more and more light, until at last a colourless liquid remained. On continuing the distillation to dryness, a slight residue of coal remained in the retort. The last and lighter portions were freed from bromine by means of water and a little potash, when they yielded a colourless, oily, aromatic liquid. This body proved on analysis to be a bromide of carbon; for 1·539 grm. yielded, when burnt with oxide of copper and with oxygen, 0·4025 carbonic acid. II. 1·2085 grm. gave 0·2985 carbonic acid. III. 1·8436 gave 0·458 carbonic acid. IV. 0·7586 grm. yielded, on ignition with lime, 1·6577 bromide of silver. No water was perceptible during the combustion. From these results, the compound consists of equivalents of bromine and carbon:—

Carbon....	7·13	6·74	6·77	..	1	7·12
Bromine ..	..	..	..	91·75	1	92·88

The specific gravity of this bromide of carbon is 2·436; it has a most agreeable, æthereal, aromatic odour, a sweet taste, and is highly refractive. Some bromine is liberated from it by the influence of the air and heat, which causes it to acquire a yellow colour and the odour of bromine. It boils at 248°. Nitric acid of 1·42 spec. grav. decomposes it but very slightly even on boiling, and it distils over almost unaltered from concentrated sulphuric acid. When treated with potash in a state of fusion, it is entirely decomposed without any elimination of carbon. It does not burn, is sparingly soluble in water, to which however it imparts odour and taste; with alcohol and æther it mixes in every proportion. It does not solidify at −13° F. Different samples of commercial bromine contained from 6 to 8 per cent. of this bromide of carbon; and it is probable that

it is formed from the æther employed in the preparation of bromine. Direct experiments, in which bromine was distilled with æther, showed that but very little, and frequently not a trace of bromide of carbon was formed; but it was procured in considerable quantity when, previous to distillation, chlorine was passed through the mixture. If, instead of pure æther, one containing alcohol or pure alcohol is employed, a larger quantity of the bromide of carbon is formed, but which frequently contains chlorine, even as much as 15 per cent.—Poggendorff's *Annalen*, lxxi. p. 297.

On the Solubility of the Chloride of Sodium in Alcohol. *By* R. Wagner.

As it is frequently important to know accurately the quantities of chloride of sodium which alcohol is capable of dissolving at different temperatures, and as no definite statements on this subject are to be found in any of the works on chemistry, I have made some experiments on the solubility of pure chloride of sodium in alcohol of 0·876 spec. grav. and 0·815, the results of which are contained in the following table:—

Alcohol of	0·876	dissolved at	57° F.	0·661 p. c.	chloride of sodium.
...	0·876	...	59° ...	0·700 ...	...
...	0·876	...	101° ...	0·736 ...	...
...	0·876	...	161° ...	1·033 ...	...
...	0·815	...	59° ...	0·174 ...	...
...	0·815	...	171° ...	0·171 ...	...

Journ. für. Prakt. Chem., May 18, 1847.

On removing Stains from Linen. *By* Messrs. T. and H. Smith.

We lately had occasion to remove some marks from linen which had been damaged by writing on it with "Marking-ink without preparation," now so much in use. In writing with this ink, to bring out the characters, the application of a sharp heat is required, and in this case the necessary heat was obtained by the use of a hot iron.

The usual means, such as cyanuret of potassium, Dr. Herapath's mode of forming an iodide of silver by means of tincture of iodine, and subsequent removal of this by hyposulphite of soda, as well as others which need not here be mentioned, proved quite ineffectual in making any impression on the marks. We at first thought that their obstinate resistance to the means of erasure employed might have arisen from the texture of the cloth having been carbonized by the action of some corrosive acid entering, through faulty preparation, into the constitution of the marking-ink. In this we afterwards found ourselves mistaken. These stains, although by the action of heat rendered so difficult to remove, may, as we found on trial, be very easily, speedily, effectually, and without the slightest danger of damaging the most delicate fabric, effaced by wetting the stains with

the common solution of chloride of lime. In the course of a few minutes these pass from black to white, in consequence of the formation of the white chloride of silver; but as this would soon again blacken by the action of light, it must be dissolved and washed entirely away. In consequence of the ready solubility of the chloride in solution of ammonia or hyposulphite of soda, this operation can fortunately be done without the least difficulty, by dipping the part of the cloth covered with the now white marks into either of these solvents, and then after a few minutes rinsing thoroughly in clean water*.

By this simple and easy process the marks may be entirely removed in a few minutes. This plan, so far as we are aware, has now been proposed for the first time; but whether this be the case or not, it is so much superior to any other known to us, that we believe you will do a service to your numerous readers by giving it a place in your Journal.—*Pharmaceutical Journal*, Sept. 1847.

ANALYTICAL CHEMISTRY.

On the Separation of Nickel from Cobalt, and of both these from other Metals. By H. Rose†.

The perfect separation of these two metals, which are nearly always associated together, is one of the most difficult problems in analytical chemistry; and the most eminent chemists of older and more recent times have proposed methods which for the most part effect the purpose very imperfectly. I will not subject the older methods to examination here, as they have for some time ceased to be employed; but I shall allow myself a few observations on those in use at the present day.

The most effectual methods of separation are those of R. Phillips, Laugier and Liebig. That of R. Phillips‡ was, until Liebig proposed a new method, the one most frequently employed. It consists essentially in the addition of ammonia in excess to the solution of the metals in which they dissolve when ammoniacal salts are present; and in the precipitation of the oxide of nickel from this

* When the marks penetrate deeply, the space of a few minutes is too short for the complete conversion of the silver into chloride, a crust of this insoluble compound being formed on the surface. The interior portions are apparently in this way protected from the further action of the solution. Even after continued action for an hour or two, the conversion is not complete. The entire destruction of that part of the fabric corresponding to the marks may ensue before this desired point shall have been reached. In these cases, the plan we have already recommended should be followed; and should the marks, after the action of the ammonia, not then be entirely obliterated, a repetition of the process will invariably succeed in removing these, without even a trace of their previous existence being left behind.

† We are indebted to our friend T. H. Henry, Esq. F.R.S., for the translation of this paper, and the valuable remarks which accompany it.—Ed.

‡ Phil. Mag. by Tilloch, vol. xvi. p. 312.

solution by means of caustic potash, while the oxide of cobalt remains in solution. This method requires caution even to obtain approximate results, especially when the quantity of cobalt in combination with the nickel is considerable; and any want of foresight may occasion considerable errors. Phillips himself remarks, that the separation only succeeds when the solution is very dilute and the quantity of ammonia is considerable. If the quantity of the ammoniacal salt and free ammonia in the solution of the metals be not very large, much oxide of cobalt is precipitated with the oxide of nickel by the potash. An unpracticed person can by no means ascertain how much of the ammoniacal salt may be required to prevent the precipitation of the cobalt completely. We may certainly recommend the addition of a very large quantity; but then an almost incredible amount of potash is often required to precipitate the oxide of nickel. It is no exaggeration to say that little less than a pound weight of potash may be required when a few grammes of oxide of cobalt are to be separated from oxide of nickel, and which nevertheless may still exhibit a trace of cobalt before the blowpipe. But even those practised in analytical operations should never consider the oxide of nickel precipitated by Phillips's method as pure. It is absolutely necessary in quantitative examinations to redissolve the oxide and repeat the process, when a further portion of oxide of cobalt will be separated from the oxide of nickel.

To ascertain the error which the employment of this method might give rise to, 0·454 grm. of metallic nickel and 0·478 grm. metallic cobalt were dissolved together in hydrochloric acid. Ammonia was added and muriate of ammonia in such considerable quantity that one would have thought it quite sufficient to prevent the precipitation of the oxide of cobalt by the caustic potash, an extraordinarily large proportion of which was required to precipitate the oxide of nickel. Notwithstanding these precautions, the startling quantity of 0·926 grm. of oxide was obtained; thus instead of 48·71 per cent. of metallic nickel, which the mixture contained, not less than 78·20 per cent. was obtained, which of course when tested by the blowpipe was found to contain much cobalt. If therefore so erroneous a result were obtained by one not altogether unskilled, such a method can only be recommended when a very small quantity of cobalt is to be separated from a considerable quantity of nickel, or when the precipitated oxide of nickel is treated over again in the same manner until it is found to be free from cobalt.

With regard to the method of Laugier*, it was not even by the author himself proposed as a method of quantitative separation, but only to be employed to obtain the metals pure from one another. It consists in dissolving the oxalates in ammonia, and exposing the ammoniacal solution to the atmosphere. On the evaporation of the ammonia, the oxide of nickel is deposited, and the oxide of cobalt remains in solution. The solution loses its blue colour, and assumes a rose colour; on continuing to expose this pink solution to the atmosphere, the oxide of cobalt is in turn precipitated, and the solu-

* Ann. de Chimie, vol. ix. p. 267.

tion becomes colourless. If therefore the solution has not been exposed sufficiently long, the cobalt solution may contain a portion of the oxide of nickel; if, on the contrary, it has been exposed too long, the oxide of nickel will contain oxide of cobalt. The objection to this method therefore is, that it is impossible to decide with accuracy when the whole of the nickel has been completely separated and the precipitation of the oxide of cobalt not yet commenced. On this account it cannot be used with advantage in quantitative analysis; but it affords a means of detecting with great accuracy the presence of oxide of cobalt in the oxide of nickel; and it is possible, by means of it, to ascertain the presence of oxide of cobalt when the quantity is too small to allow of its detection by the blowpipe. It is only necessary for this purpose to dissolve a very minute quantity of oxalate of nickel in ammonia in a test-glass, and to allow it to stand, observing it from time to time. A rose-pink solution will often be remarked when an oxide of nickel has been used which was previously considered as pure. It is more difficult to detect traces of nickel in oxide of cobalt by this method. Laugier however detected a minute trace of nickel in the cobalt glance from Tunaberg, which was previously considered to be free from it.

Of all the methods employed hitherto, that of Liebig* affords, without doubt, the most accurate results, but only when many precautions are observed. According to the method of Liebig, hydrochloric acid is added to the solution of the metals, and afterwards cyanide of potassium in such excess that the precipitate at first formed is redissolved. Cobalticyanide of potassium is formed by separation of hydrogen, the solution of which is not decomposed either by acids or alkalies. Hereupon hydrochloric acid is added to the solution, which is then boiled until the odour of hydrocyanic acid is no longer perceptible. The nickelocyanide of potassium is by this means converted entirely into chloride of nickel, and may now be precipitated from its solution by means of caustic potash as oxide of nickel. The determination of the cobalt however is more difficult. The solution filtered from the oxide of nickel must be mixed with nitric acid and evaporated to dryness, and the dry mass kept some time in a state of fusion. By fusion with nitrate of potash, the cobalticyanide of potassium is at length decomposed; and on treating the melted mass with water, the oxide remains behind, and may be reduced by hydrogen in the usual manner. It is necessary, in using this method, to precipitate the oxide of nickel by a considerable excess of caustic potash, and to boil the solution with it a long time; otherwise it has not the green colour peculiar to the hydrated oxide of nickel. It is important that the precaution of redissolving the oxide of cobalt, and precipitating it by caustic potash, should not be omitted. The fusion of the cobalticyanide of potassium can only be performed in a porcelain crucible, which, even when of the best Berlin manufacture, is strongly acted on. Portions of the porcelain remain behind undissolved when the oxide is redissolved in muriatic acid. That this method however gives satisfactory results when

* Annalen der Chemie und Pharmacie, vol. xli. p. 285.

pursued with care, will be seen from the following experiment conducted by M. Weber:—

0·721 grm. of metallic cobalt and 0·532 grm. oxide of nickel were dissolved in hydrochloric acid, and treated according to Liebig's method. 0·710 grm. metallic cobalt and 0·567 oxide of nickel were obtained, or per cent.—

	Quantity used.	Quantity obtained.
Cobalt	63·25	62·28
Nickel.....	36·75	39·12
	100·00	101·40

It will be seen that by this method a degree of accuracy may be attained which is not possible by the others. The experiment described above however was that which afforded the most accurate results. Many of M. Weber's earlier quantitative experiments gave results wide of the truth. He often obtained apparently less nickel and much more cobalt than the substances employed really contained. In any case however the determination of the oxide of cobalt by this method is exceedingly inconvenient. The evaporation of the liquid filtered from the oxide of nickel, after it has been rendered acid by the addition of nitric acid, is attended with difficulty, owing to the separation of the salts, which are present in considerable quantity, and render the employment of the greatest attention necessary in order to avoid a loss from their efflorescence or decrepitation.

During many years, even before the publication of Liebig's method, I have been employed in the quantitative separation of cobalt and nickel; but my earlier results were all in the highest degree imperfect, and were far from attaining that degree of accuracy which is possible by the employment of the method of Liebig. It appeared to me probable, at an early period of the investigation, that a method for the separation of the two metals might be grounded upon the much greater tendency in the protoxide of cobalt than in the protoxide of nickel to pass to a higher degree of oxidation. Several chemists have attempted the separation of these two metals in this or a similar manner. The oxides were converted into the black superoxides, and these treated with reagents, by which the peroxide of nickel only was reduced to the state of protoxide and dissolved in the reagent employed; or the precipitated protoxides were treated with chlorine, by which chloride of nickel was formed and dissolved, and superoxide of cobalt, which remained behind undissolved. The former of these methods was employed by Thenard. He treated the freshly-precipitated oxides with chloride of lime, and afterwards the superoxides produced with ammonia, which dissolved out the oxide of nickel, leaving the superoxide of cobalt undissolved. The second method was made use of by Berthier*, not for a quantitative separation, but merely in the preparation of pure metallic nickel. He remarks, that when the quantity of the cobalt preponderates over that of the nickel, the solution of chloride of nickel will

* Annal. de Chimie, vol xxv.

contain cobalt; and that when the nickel preponderates, the superoxide of cobalt will contain nickel.

In my first experiments I converted the oxides precipitated by potash into superoxides by means of gaseous chlorine, and treated these with acetic acid. As is well known, this is the only acid capable of dissolving the superoxide of cobalt without decomposition. The superoxide of nickel is dissolved, forming a green solution, which contains the protoxide. If both superoxides be acted upon at the same time by acetic acid, in many cases oxide of nickel is first dissolved, forming a green solution; and a mixture of both superoxides remains, which on continued digestion dissolves to a deep brown solution. I frequently obtained this solution at once; but it contained not only superoxide of cobalt, but also superoxide of nickel, for on treating it with carbonate of baryta in the cold, both were precipitated.

When I treated a neutral solution of oxide of nickel with gaseous chlorine, and then added carbonate of baryta to it, I did not obtain the black precipitate of superoxide of nickel immediately, but only when it had stood a long time, and then only in small quantity. A neutral solution of oxide of cobalt, treated first with chlorine and afterwards with carbonate of baryta, deposits the whole of its cobalt as superoxide. An approximate separation may be effected by this method. If carbonate of baryta be added to a neutral solution of the two oxides, and afterwards chlorine passed through it, both metals are precipitated as peroxides, the cobalt first, and afterwards more slowly the nickel. If hydrochloric acid be added to a neutral solution of chloride of cobalt, and then a current of chlorine passed through it, its pink colour is very slightly altered; it becomes a little brownish; but the whole of the chloride is converted into superchloride, and carbonate of baryta precipitates from the solution the whole of the cobalt as superoxide. If a solution of chloride of nickel be treated in the same manner after the addition of hydrochloric acid, no precipitate is produced by carbonate of baryta even after standing some time. In case the quantity of hydrochloric acid added was very small, a minute quantity of black superoxide of nickel may be precipitated after standing twelve hours.

Upon these facts, viz. that in a solution of oxide of cobalt containing free hydrochloric acid the whole of the metal is converted into the superoxide by means of chlorine, while the chloride of nickel remains unaltered in the acid solution, I based a method for the separation of the metals, which after so many failures afforded me results which surpassed my expectations, and attained a degree of accuracy not often arrived at even in the separation of metals which do not possess that close analogy presented by cobalt and nickel. The method is the following:—Both metals are dissolved in hydrochloric acid; the solution must contain a sufficient excess of free acid; it is then diluted with much water; if 1 or 2 grms. of the oxides are operated on, about 2 lbs. of water are added to the solution. As cobalt possesses a much greater colouring power than nickel, not only in fluxes but also in solutions, the diluted solution

is of a rose colour, even when the quantity of nickel present greatly exceeds that of the cobalt. A current of chlorine gas is then passed through the solution for several hours; the fluid must be thoroughly saturated with it, and the upper part of the flask above the liquid must remain filled with the gas after the current has ceased. Carbonate of baryta in excess is then added, and the whole allowed to stand for twelve or eighteen hours, and frequently agitated. The precipitated superoxide of cobalt and the excess of carbonate of baryta are well-washed with cold water, and dissolved in hot hydrochloric acid; after the separation of the baryta by sulphuric acid, the cobalt is precipitated by hydrate of potash, and after being washed and dried is reduced in a platinum or porcelain crucible by hydrogen gas. The fluid filtered from the superoxide of cobalt is of a pure green colour. It is free from any trace of cobalt. After the removal of the baryta by means of sulphuric acid, the oxide of nickel is precipitated by caustic potash. Even this method did not give exact results on the first trial. 0·318 grm. metallic nickel and 0·603 grm. metallic cobalt were employed, and 0·430 grms. oxide of nickel and 0·580 grm. cobalt were obtained:—

	Employed.	Obtained.
Nickel	34·53	36·75
Cobalt	65·47	62·98
	100·00	99·73

The cause of these incorrect results is, that the solution was filtered an hour or two after the precipitation of the superoxide of cobalt by the carbonate of baryta. It is necessary however to wait a considerable time, at least twelve hours, or even eighteen is better, and allow the excess of carbonate of baryta to remain in contact with the solution, as the superoxide of cobalt is precipitated very slowly; this explains the diminution of the cobalt and increase of the nickel in the above experiment.

In another experiment, in which this source of error was avoided, 0·739 grm. metallic nickel and 0·540 metallic cobalt were used, and 0·548 grm. cobalt obtained, that is 42·84 per cent. instead of 42·22. The nickel was not determined. Two experiments were made by M. Weber. In one, 0·818 grm. cobalt and 0·980 grm. nickel were taken, and 0·806 grm. cobalt and 1·274 oxide nickel obtained.

	Used.	Obtained.
Cobalt	45·50	44·77
Nickel	54·50	55·83
	100·00	100·60

In the second, 0·516 grm. metallic cobalt and 0·637 oxide of nickel were taken, and 0·517 grm. cobalt obtained.

It will be seen from these experiments, that on the proper precautions being taken very accurate results may be obtained by this method. It has also this advantage, that it is equally applicable whatever the relative proportions of the cobalt and nickel may be.

This or a similar method may be employed with advantage on

a large scale, to procure cobalt and nickel in the purest state. Both metals are much more employed in the arts now than formerly; and in many cases it is important to prepare them as pure as possible. This is the case when oxide of cobalt is to be employed in painting on porcelain, when a very small portion of nickel seriously affects the purity of the blue tint to be obtained by it. I have at least prepared the pure oxides of nickel and cobalt used in my laboratory in this manner; and in the experiments described above, none but the oxides so prepared were used. The nickel which occurs in commerce contains besides traces of arsenic, cobalt, copper and iron. It should be dissolved in hydrochloric acid, and the cobalt and iron separated by treatment with chlorine and carbonate of baryta, and then the copper precipitated by sulphuretted hydrogen.

It will be readily perceived, that not only cobalt, but also other metals, as iron and manganese, may be separated from nickel by this method. On the other hand, oxide of cobalt may be separated from the oxide of zinc, and other strongly basic oxides, which are not converted into superoxides. Nickel and cobalt can moreover be separated from metals, to which they bear a close analogy in various ways. I have given a method in my 'Manual of Analytical Chemistry,' by which both these metals may be separated from manganese, viz. by converting them into chlorides, and treating these by hydrogen, which reduces the chlorides of nickel and cobalt to the metallic state, but not the chloride of manganese. This method affords accurate results, but is rather complicated. Völker* has remarked, that at a very strong heat the chloride of manganese is slightly volatile. Although this is inappreciable except when the heat has been raised too high, still it is possible to effect their separation by simpler methods.

With many other chemists, I have convinced myself that the method of Barreswil† for the separation of the oxides of cobalt and manganese, by adding carbonate of baryta to the solution, and passing a current of sulphuretted hydrogen through it, is not applicable, since, as indeed might be seen *à priori*, not only the oxide of cobalt, but also the oxide of manganese will be precipitated as a sulphuret.

From nickel the manganese may be best separated in the same manner as cobalt, as I have remarked above. Manganese may be separated from both of them, however, by a method which, in its essential parts, was proposed by Wackenroder‡. It is based upon the fact, that although nickel and cobalt are not precipitated from their solutions by sulphuretted hydrogen, especially when they are slightly acid, still the sulphurets precipitated by hydrosulphate of ammonia are not dissolved by very dilute hydrochloric acid. I long ago, in the first edition of my 'Manual of Analytical Chemistry,' directed attention to this curious property, and made use of it for qualitative experiments, but at that time had not availed myself of it in quantitative separations. When the oxides are contained in

* Annalen der Chemie und Pharmacie, vol. lix. p. 33.
† Chem. Gaz. vol. iv. p. 159.
‡ Annalen der Chemie, vol. li. p. 219.

an acid solution (which should not contain nitric acid however), it is made ammoniacal, and they are precipitated as sulphurets by hydrosulphate of ammonia. Very dilute hydrochloric acid is then added to the solution until it has a very slightly acid reaction; the sulphurets of nickel and cobalt remain undissolved; they are washed with water containing a little sulphuretted hydrogen and a trace of hydrochloric acid. The sulphuret of manganese is dissolved with facility; but although the fluid filtered from the sulphurets of nickel and cobalt gives only a rather dirty flesh-coloured precipitate on the addition of ammonia and hydrosulphate of ammonia, still the sulphuret of manganese contains small quantities of sulphuret of cobalt or nickel; and when therefore it is treated anew with very dilute hydrochloric acid, minute quantities of the black sulphurets remain behind. By this repeated treatment, a very nearly correct separation may be obtained; but the results are more satisfactory in the separation of cobalt from manganese than of nickel from the latter metal, evidently because nickel is not very perfectly precipitated by hydrosulphate of ammonia. 0·300 grm. of metallic cobalt and 0·385 grm. of deutoxide of manganese gave—after the sulphuret of cobalt had been converted by *aqua regia* into oxide, and this precipitated by hydrate of potash, and after the chloride of manganese dissolved was freed from sulphuretted hydrogen and precipitated by carbonate of soda—0·302 metallic cobalt and 0·392 oxide of manganese.

0·251 grm. of oxide of nickel and 0·296 grm. oxide of manganese treated in the same manner gave 0·214 oxide of nickel and 324 oxide of manganese*.

Iron also may be separated from nickel, and better still from cobalt, in the same manner as manganese, since sulphuret of iron, like sulphuret of manganese, is easily soluble in very dilute hydrochloric acid; but in this case the re-solution of the sulphuret of iron is likewise necessary. 0·425 grm. metallic cobalt and 0·170 grm. sesquioxide of iron, when treated in this manner, gave 0·414 grm. metallic cobalt and 0·172 sesquioxide of iron.

I have already stated, in the last edition of my 'Manual of Analytical Chemistry,' that the oxide of zinc may be completely precipitated from its solution in acetic acid by means of sulphuretted hydrogen when no strong inorganic acid is present, even though the solution contain a large excess of acetic acid; and recommended the separation of this oxide from alumina, the oxides of iron, manganese, and even from those of cobalt and nickel, by this method. This method also succeeds when a considerable addition of acetic acid is made to the solution, especially if the latter oxides are present.

From alumina oxide of nickel may be separated by fusing them together with hydrate of potash in a silver crucible; on treating the fused mass with water, the oxide of nickel remains behind in a dense state. It weighs rather more than the oxide employed, but contains no alumina, and potash must therefore be present. 0·238 grm. oxide of nickel mixed with alumina weighed, after it had been treated in this manner, 0·245 grm. By boiling with a solution of

* According to Liebig and Fresenius, manganese may likewise be separated from cobalt and nickel by cyanide of potassium.

potash nickel cannot be separated from alumina when both are contained in a solution, not even when the treatment is repeated. When the 0·245 grm. was dissolved in hydrochloric acid with the help of a little sulphuric acid, and the separated solution of alumina in potash, to which more potash was added, mixed with the solution, and the whole boiled, the oxide of nickel separated weighed 0·320 grm. When this was dissolved in hydrochloric acid, a considerable quantity of alumina separated on the addition of ammonia in excess. As, however, the fusion of hydrate of potash in a silver crucible is attended with inconvenience, and the oxide of nickel obtained requires to be dissolved and precipitated anew, the separation of these oxides by means of carbonate of baryta is preferable.

I have tried in vain, by fusing with a fixed alkaline carbonate, to separate quantitatively alumina from the oxides of cobalt and nickel, and from those of other metals which are incapable of expelling the carbonic acid from an alkaline carbonate at an elevated temperature. It is difficult to obtain a perfectly clear solution by fusing alumina with carbonated alkali, and treating the melted mass with water; it is quickly rendered turbid by the carbonic acid of the atmosphere. A fused mass is much more easily obtained with carbonate of soda than with carbonate of potash.

Observations on the preceding Article. By T. H. Henry, F.R.S.

I take the opportunity afforded by the publication of the above interesting paper of Prof. Rose to communicate a few experiments made some months ago by myself on the same subject. With regard to the process of Liebig, I have never succeeded in preventing a portion of the oxide of cobalt from being precipitated with the oxide of nickel; and I am inclined to think that the cobalticyanide of potassium is not so difficult of decomposition by acids as has been supposed, and that in this respect it behaves in some degree like the analogous ferridcyanide of potassium*. I dissolved 100 grs. of oxide of cobalt, in which no trace of nickel could be detected by the blowpipe, in hydrochloric acid, added sufficient cyanide of potassium to redissolve the precipitate at first formed, and evaporated the solution at a very gentle heat with sulphuric acid in excess nearly to dryness; it was then diluted with water, neutralized with carbonate of soda, and boiled a few minutes with hydrate of soda; the precipitate washed, dried and ignited, weighed 16 grs.; these 16 grs., treated in the same manner, gave a precipitate which weighed 3 grs., and was at any rate chiefly oxide of cobalt, as it gave an intensely blue glass with borax.

I then took 50 grs. of the same oxide, and used a considerable

* A portion of cobalticyanide of potassium was dissolved in water, a little hydrochloric acid added to the solution, and the whole evaporated to dryness in a water-bath; the solution became of a deep yellow colour and evolved hydrocyanic acid; the dry mass was dissolved in a little water and treated with alcohol, the undecomposed cobalticyanide was precipitated, and a portion of chloride of potassium dissolved, for on evaporating the alcoholic solution to dryness and redissolving the residue in water, abundant precipitates were produced on the addition of nitrate of silver and chloride of platinum.

excess of cyanide of potassium, and boiled the solution with hydrochloric acid in excess for about six hours, following strictly the process given in Fresenius' 'Analyse,' p. 250, but obtained a precipitate which weighed 9 grs., and in which I could not detect a trace of nickel.

I next prepared, according to the directions given by Gmelin (Berzelius, vol. iii. p. 643–5 Auflage), some cobalticyanide of potassium, and purified it by repeated crystallization. It was, as described by Liebig (in the sixth edition of Turner's 'Chemistry'), in slightly yellow prismatic crystals, which were anhydrous, and fused on the application of heat to a bluish-green fluid; the solution was colourless, neutral to test-paper, and precipitated the salts of protoxide of cobalt of a rose colour, and the protosulphate of iron of a white colour (Liebig says it does not precipitate the salts of iron; I presume he means the persalts).

10 grs. of this salt were dissolved in muriatic acid, diluted with twice its weight of water, and boiled for about half an hour, adding water occasionally; the solution became yellow, and smelt strongly of hydrocyanic acid; it was saturated with carbonate of soda, and boiled a few minutes with hydrate of potash; a bluish-green precipitate was produced, which was well washed and ignited, and weighed 0·19 gr.; it was oxide of cobalt, and imparted an intense and pure blue colour to borax; this quantity corresponds to very nearly 10 per cent. of the amount of cobalt contained in the salt. I hope shortly to be able to explain the exact nature of the decomposition which occurs; but in the meantime I think these experiments show how the excess of nickel in the analysis quoted by Prof. Rose, amounting, as will be seen, to nearly $2\frac{1}{2}$ per cent., was produced. It is probable that the nickelocyanide of potassium is first decomposed, and upon continuing the ebullition with acids, that a portion of cobalticyanide of potassium is also decomposed, which will account for the different results obtained; for it is impossible to ascertain, as Rose remarks with regard to the process of Laugier, when all the nickelocyanide is decomposed and the decomposition of cobalticyanide has not yet begun.

As in the process of Rose the passing of chlorine gas through a solution for some hours is exceedingly tedious and unpleasant to those who have not a well-appointed laboratory at their disposal, I endeavoured to obtain the same effect by a solution of bromine. I took 4·92 grs. of pure metallic cobalt and 4·61 of oxide of nickel, which was kindly furnished me by Mr. R. Phillips, and was absolutely pure; I added the solution of bromine to the acid solution of the metals, diluted as directed by Rose, until it smelt strongly of it, then carbonate of baryta in excess, and filtered after allowing it to stand twenty-four hours; I obtained 4·90 grs. of cobalt, and afterwards 4·55 grs. of oxide of nickel.

A process for the separation of these two metals has recently been given by Plattner in the second edition of his very valuable work, 'Die Probirkunst mit dem Löthrohre,' Leipsic, 1847. He precipitates the oxides together, and after igniting them mixes a decigramme with arsenic, and heats the mixture in a glass tube, then

fuses the arseniurets obtained together on charcoal, and retains the globule in the interior flame of the blowpipe until the excess of arsenic is volatilized; the subarseniurets are weighed, then treated with borax in the oxidating flame until the whole of the cobalt is oxidized and dissolved in the flux, and the subarseniuret of nickel remains free from cobalt, and can be weighed; its weight is deducted from that of the mixed arseniurets, and the proportion of both metals calculated. I have not been able to obtain very accurate results by this method, which must greatly depend upon the skill of the operator for its success. 0·462 grs. cobalt and 0·388 grs. nickel gave me 0·502 cobalt and 0·322 nickel, which is not a very close approximation.

On a new Method of detecting Potash and Soda by the Blowpipe in the Presence of Magnesia. *By* Edward J. Chapman*.

Magnesia, potash and soda being usually brought together in the analysis of inorganic compounds at the close of the process, and the detection of the latter bodies occasioning some little trouble in rapid examinations, the following method of ascertaining their presence, without the necessity of first separating the magnesia, may at times be found serviceable:—

1st, a small quantity of boracic acid (perfectly pure) is to be fused before the blowpipe in a loop of platinum wire; 2nd, a portion of the compound under examination, with a particle of oxide of copper, is then to be added to it; and 3rd, the whole subjected to an oxidating flame. If magnesia alone be present, the greater portion of it will remain undissolved, together with the oxide of copper, in the flux, the bead continuing colourless; if, on the contrary, potash or soda be mixed with the magnesia, these bodies will be immediately dissolved by the boracic acid, forming borate of potash or soda, in which the oxide of copper dissolves, communicating to the compound its peculiar colours, the bead becoming green whilst hot and blue when cold.

If the alkaline salt be in excess, the magnesia will be also dissolved. If the contrary be the case, the coloration from the dissolved oxide of copper will still be effected; but the magnesia will be perceived in the centre of the globule as a white or light-coloured insoluble mass.

It must be observed that salts of baryta or strontia fuse likewise with boracic acid, giving rise to borate of baryta or strontia, in which, as in the alkaline borates, oxide of copper dissolves, producing a green or blue coloration. If present therefore in the magnesia compound, these bodies must be removed by sulphuric acid before attempting to ascertain the presence of the alkalies by the above method. We can finally examine a fresh portion of the assay matter for potash by chloride of platinum, and for soda by the production of its well-known yellow flame.

I have not had an opportunity of examining the action of boracic acid on lithia or its salts. There can however be little doubt but

* Communicated by the Author.

that it is analogous to the action of this flux on the other alkaline bodies, and that oxide of copper dissolves in borate of lithia with the same effect.

On the Estimation of the Amount of Carbon in Cast Iron. *By* MM. KUDERNATSCH *and* HUMMEL.

The authors tested Regnault's method of burning the cast iron with a mixture of chromate of lead and chlorate of potash, and compared the results with others obtained by merely burning it with chromate of lead or oxide of copper. From their experiments, it follows that the most accurate results may be obtained by pulverizing the cast iron in a steel mortar, mixing it with a sufficiently large quantity of oxide of copper, and burning it, without the addition of any other substance capable of yielding oxygen more readily, as the combustion is perfect, and errors likely to result from any chlorine being eliminated with oxygen on employing the chromate of lead and chlorate of potash, and which would increase the amount of carbon, are avoided.—*Journ. für Prakt. Chem.*, xl. p. 499.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Process for manufacturing White Lead or Carbonate of Lead, invented by M. GANNAL.

THE difficulties which are known to exist in the manufacture of white lead by the processes now in use, and the dangers to which the workmen employed in it are exposed, determined me to undertake a series of experiments, in order to discover a process more simple and without danger to the workmen.

I feel truly happy in being able to announce to the Academy that I have succeeded in my attempts. *By an extremely simple process, in a very short time, and without any danger*, I manufacture any quantity of white lead that commerce may require, and my product will bear comparison with the most perfect that is made.

Among the chemical and mechanical processes thus far known, for the manufacture of white lead, not one appeared to me to combine the conditions necessary to obtain this product with œconomy and without great danger to the workmen. A patent taken out in 1834 by Mr. Walker Wood, points out a method, some parts of which indeed seem to be new; but the descriptions of this patent are so obscure, and at the same time so erroneous, that I have not thought it worth while to dwell on it.

The following is the description of the manner of proceeding, by which I arrived at a good result:—A hexagonal or octagonal leaden cylinder is to be prepared, 2 metres in length, with a diameter of

from 30 to 40 centimetres. The lead should be from 5 to 8 millimetres in thickness. This cylinder is to be enclosed in a frame made of rod iron, to one end of which a crank is to be attached. It is to be placed on a stand, so as to receive with ease a rotary movement. At the centre of the cylinder there is to be an opening or bung-hole, through which the materials are to be introduced. At the end opposite the crank and in the axis of the cylinder another opening is to be made, of from 3 to 4 centimetres in diameter, through which is to pass, without closing or stopping it up, an elastic tube fitted to a bellows. This tube must reach the bottom of the cylinder. 100 kilogrms. of granulated lead and 30 litres of water are to be introduced into the cylinder, the bung-hole is to be closed, and the apparatus is ready to operate. In this state, if the lateral opening is closed and the apparatus turned round at the rate of forty-five or fifty turns per minute, and if this motion is continued for five hours, about two-thirds of the lead will be found reduced to an impalpable powder, and still retaining its metallic colour. If the lateral opening remains open, then the lead so divided becomes oxidated, and the product taken out is a protoxide or massicot hydrated in part. Lastly, if an elastic tube reaching to the bottom of the cylinder is fitted to the apparatus, the other end of which is attached to a bellows receiving air from a close chamber or enclosure in which there is burning charcoal, the finely-divided lead coming in contact with the air and the carbonic acid blown into the apparatus by means of the bellows is converted into oxide, and finally into carbonate of lead or white lead.

Acting on this principle, we manufactured a considerable quantity of a product, which was judged to be equal in quality to the best of that met with in commerce.

When the cylinder has been turned for a sufficient length of time, the bung is to be opened, and the liquid contained suffered to run out; a quantity of water equal to that first introduced is put in, the cylinder is to be turned for five minutes, this second portion of liquid is to be run off, then the apparatus may be immediately recharged for a second operation, introducing however only 75 kilogrms. of lead, inasmuch as there remain 25 to 30 kilogrms. not finely divided. In order to facilitate and hasten the operation, we have made use of two different processes. The first consists in pouring into the water, at the moment of charging the apparatus, 500 grms. of nitric acid; the second, in substituting for the acid 1 kilogrm of nitrate of lead. It is however to be remarked, that during the operation a little nitrous acid is disengaged, and that when the operation is completed scarcely any is to be found in the mixture that remains. I have observed that the acid or the salt of lead is decomposed. A subhyponitrate is doubtless formed, which is afterwards decomposed by the carbonic acid. The liquid product withdrawn from the cylinder is poured into a vessel containing eight or ten times the proportion of water made use of in the operation. This mixture, violently agitated, becomes considerably whiter in proportion to the blue tint of the product taken out of the cylinder, which is occasioned by a

quantity of lead, finely divided but not yet oxidated or yellowish, if formed of oxide not carbonated.

It is to be observed, that after two days washing, the whole of the product is of the most dazzling whiteness. However, I would here observe, that having dried immediately some white lead which still contained about one-eighth of its weight of divided and non-oxidated lead, at the end of two months the entire mass had a homogeneous tint.

As in this operation some portions of granulated and others of imperfectly divided lead escape from the apparatus, it is necessary to let them deposit in vessels having openings at different heights. In the first place, the clear water which floats above the deposit is drawn off, then, by an opening somewhat lower down, the pasty deposit, which rests on the imperfectly divided particles of lead. The pasty mass is thrown on filters of closely-woven cloth, which have been previously fixed on frames. Here a large quantity of water drains off, and leaves a plastic residuum. In this state the filters are taken down, the ends of the cloth are folded over, and the whole is subjected to a violent pressure. When this pressure has removed the greatest quantity of water possible, the packets are taken out, the cloths are taken off, the mass is divided into pieces of the desired form, and they are then placed in a hot-air stove. As may be seen, the theory of this operation is as simple as its manipulation. In adopting this system of manufacture, we have *simplification of labour, a larger product, saving of manual labour, and less chance of loss.*

Until the present period, our manufacturers, followers of blind routine, imitated the form which the Dutch formerly gave to this article; but now our workmen, our foremen, are too well informed to pay any attention to the particular form or shape that may be given to a product; and when they learn that the adoption of this new form or shape has for its principal object the preservation of the health and life of many thousands of fathers of families, who annually perish in consequence of the fatal results of the present mode of manufacture, they will doubtless applaud the intention of my publication, and will hasten to call for white lead in a new form.

To sum up the whole, my process of manufacture consists—

1. In granulating the lead.
2. In reducing it into indefinitely fine particles by friction on itself in a leaden cylinder.
3. In facilitating the oxidation of the lead so divided by the introduction of atmospheric air into the apparatus.
4. In *carbonating* immediately this oxide of lead by making use of air more charged with carbonic acid.
5. In hastening the oxidation of the lead, by introducing into the apparatus nitric acid or the nitrate of lead.
6. In washing the product obtained by this process.
7. In hastening its desiccation, by subjecting the result to the greatest possible pressure.

8. In dividing by square points the pressed mass.

9. In drying in a hot-air stove the divided product.

On the 24th of December 1839 a room and the closet of an apartment still occupied by M. Mequignon, Jun., Rue des Grands Augustins, No. 9, were painted by Mr. Coulon with white lead manufactured by me by this process; this paint, after four years, is as beautiful as when it was first applied.

The publication now made is entirely for the benefit of the workmen. The manufacturers will hasten to adopt it; but I think, moreover, that taking into view public health, the government ought immediately to interdict the method of making it by putting the lead into pots, which is the principal source of the painters' or lead cholic. —*Journal of the Franklin Institute*, July 1847.

PATENT.

Patent granted to Charles Reinhold Lothman, Craven Street, Strand, *for Improvements in the Manufacture of White Lead.*

This invention consists in manufacturing white lead, by submitting lead to the action of the acids or vapours produced in the operation of brewing, or in the manner hereafter described.

The process of manufacturing white lead, according to this invention, is carried on in an air-tight chamber, 6 feet high, 6 feet long and 6 feet broad, having a flue at the lower part of it, connected with a furnace, by means of which the chamber can be heated to from 72° to 96° F. All round the chamber, at distances of about 5 feet apart, wooden posts are fixed, reaching from the bottom of the chamber to the top; to these posts a number of pieces of wood are fastened, at distances of about 1 foot apart, for the purpose of supporting other pieces of wood, 1 inch square, and extending from one end of the chamber to the other; on these last-mentioned pieces 5 cwts. of lead are hung in sheets, 2 feet long, 1 foot wide and $\frac{1}{16}$th of an inch thick. On the floor of the chamber is placed a tub, containing 8 pecks of malt, 2 lbs. of sugar, 6 pints of yeast and 12 gallons of water, and the interior of the chamber is heated to the degree above mentioned; this temperature is to be maintained until the lead is converted into white lead. The mixture in the chamber undergoes fermentation; and after the vinous fermentation has ceased and the liquid becomes mouldy, it is drawn off into vessels, in which it is mixed with 2 gallons of vinegar, and heated by steam; it is then gradually introduced through a pipe into the chamber. After the mixture is taken out, a fresh supply is to be introduced. The lead is by these means converted into white lead.

The patentee states, that he claims the use of the acids or vapours produced in the process of brewing, or the acids or vapours evolved in breweries, by introducing them into the chamber through a pipe fastened to the vats or vessels in which they are generated. He also claims the use of atmospheric air, by pumping it into the said chamber by an air-pump.—Sealed Jan. 7, 1847.

THE CHEMICAL GAZETTE.

No. CXIX.—October 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Distribution of the Inorganic Substances in the different Parts of Plants. *By* Dr. C. Rammelsberg.

The examination of two important cultivated plants, rape and peas, with respect to their inorganic constituents or those substances which the plant takes from the soil, which must consequently contain them, led to the very interesting result, that the substances contained in the *seed* differ in quality and quantity from those contained in the other parts of the plant or the *straw*. This peculiar function of the different organs of the same plant, of selecting the mineral substances presented to it in the soil, does not appear to have hitherto attracted sufficient attention.

The *seed* of the rape and peas which I had occasion to examine contained *only potash*, not a trace of soda; the *straw*, on the contrary, yielded both alkalies, but by far the larger portion was *soda*. The soil upon which these plants were grown contained both alkalies; but potash alone was requisite for the formation of their seed, and had collected in them in considerable quantity. Both plants contained *lime* and *magnesia*; the former predominated in the straw, the latter in the seed. The *phosphoric acid*, the principal constituent of the seed, was only present in small quantity in the straw; the rape-seed, for instance, contained 8 times, the peas $3\frac{1}{2}$ times as much phosphoric acid as an equal weight of straw of the plants. The reverse is the case with the *metallic chlorides* and *sulphates*, which occur in the straw in considerable abundance, and only in small quantity in the seed. The same applies with respect to *carbonic acid*, which is produced from organic acids, or other electro-negative bodies (albumen, &c.), on charring the substances. Their amount may depend, it is true, upon the temperature employed; but when this, as in the present case, was as nearly as possible the same, it cannot be merely accidental that rape-straw contains nearly 8 times, pea-straw 22 times as much carbonic acid combined with inorganic bases as the respective seeds. The following tabular arrangement of the inorganic constituents will render these relations more evident:—

	Rape.		*Peas.*	
	Seed.	Straw.	Seed.	Straw.
Potash	25·18	8·13	43·09	8·20
Soda	..	19·82	..	12·50
Lime	12·91	20·05	4·77	30·53
Magnesia	11·39	2·56	8·06	6·93
Peroxide of iron	0·62			
Phosphoric acid	45·95	4·76	40·56	9·21
Sulphuric acid	0·53	7·60	0·44	7·01
Carbonic acid	2·20	16·31	0·79	17·36
Muriatic acid	0·11	19·93	1·96	7·15
Silicic acid	1·11	0·84	0·33	0·62

Quantity of ash from 100 parts of substance:—

Rape	Seed	4·54
	Straw	5·21
Peas	Seed	3·28
	Straw	4·15

In these experiments, the vegetable substances were charred at a very gentle heat in a covered crucible, in order to prevent any decomposition and loss, and the analysis conducted in the manner recently described by Prof. H. Rose in this Journal*. Of the 100 parts above-mentioned the portion soluble in water consisted of—

	Rape.		*Peas.*	
	Seed.	Straw.	Seed.	Straw.
Potash	3·08	7·53	7·47	6·74
Soda	..	18·63	..	9·90
Lime	..	..	0·03	0·29
Magnesia	..	..	0·15	0·15
Phosphoric acid	1·74	..	2·10	0·64
Sulphuric acid	0·53	7·60	0·44	5·30
Carbonic acid	0·42	4·77	0·79	4·75
Muriatic acid	0·11	19·93	1·96	7·15
	5·88	58·46	12·94	34·92

How far this difference in quantity of the constituents in seed and straw extends to other vegetables, will be seen from the following analyses of some of the most important; it is, however, unfortunate that parts of the same plants cannot be compared more frequently.

Indian Corn.

	Seed. Letellier.	Straw. Hruschauer.	
Potash	30·8	12·94	4·56
Soda		38·74	12·41
Phosphoric acid	50·1	10·52	21·40
Carbonic acid	..	9·49	4·37

* See page 158 of the present volume.

Wheat (*parts of the same plants*).

	Petzholdt.	
	Seed.	Straw.
Potash	25·81	15·48
Soda	2·68	3·13
Lime	1·49	3·50
Magnesia	12·18	
Phosphoric acid	57·31	4·08
Sulphuric acid	0·03	0·94
Silica	0·33	72·43

Rye.

	Seed.			Straw.
	Will and Fresenius.	Bichon.	Gerathe-wohl.	Will and Fresenius.
Potash	31·89	11·43	30·36	17·03
Soda	4·33	18·89		
Lime	2·84	7·05	3·06	8·98
Magnesia	9·86	..	11·33	2·39
Phosphoric acid	46·03	51·81	45·39	3·80
Silica	0·17	0·69	4·29	63·89

Barley (*parts of the same plant*).

	Way.	
	Seed.	Straw.
Potash	19·1	24·4
Soda	..	1·0
Lime	3·6	9·6
Magnesia	7·6	1·7
Chloride of sodium	2·3	8·25
Phosphoric acid	31·2	1·8

Other analyses of the seed have yielded—

	Köchlin.	Bichon.	Schmidt.
Potash	13·30	3·91	20·91
Soda	6·53	16·79	

Oats.

	Seed.			Salm-Horstmar.	
	Boussin-gault.	Knop and Schned.	Straw. Levi.	Seed*.	Straw*.
Potash	12·9	13·6	12·18	20·40	43·90
Soda	..	..	14·69	1·90	4·00
Lime	3·7	1·3	7·29	3·15	4·84
Magnesia	7·7	8·6	4·58	14·30	3·44
Phosphoric acid	14·9	16·5	1·94	42·54	0·51
Chlorine	..	..	..	..	6·80
Sulphuric acid	..	..	..	1·70	4·50

* Grown in soil containing no humus.

The same relations occur in woody plants, for instance in—

Pinus picea.

	Seed. Poleck.	Wood. Levi.
Lime	1·54	46·15
Phosphoric acid	39·65	4·49

Pinus sylvestris.

	Poleck.	Böttinger
Potash	22·37	0·72
Soda	1·26	12·30
Lime	1·86	27·87
Phosphoric acid	45·95	1·00

A glance at these numbers shows that it is evidently not yet time to seek for any law in the distribution of the constituents. Admitting the correctness of the statements, especially with respect to the relative quantities of the two alkalies, only the oats, and perhaps the barley, among the Cerealia exhibit the same relations which were found in the rape and peas. The phosphoric acid alone occurs everywhere without exception to a great amount in the seed; on the contrary, in the other parts of the plants in very small quantity; and, as in the rape and peas, the lime in the straw or wood exceeds the magnesia in the seed. Further experiments on the seed and other parts of the same plant will undoubtedly show what inorganic substances they require, and whether in vegetables from different localities there is any replacement of one substance by another.—Poggendorff's *Annalen.*

Researches on the Bile. By Prof. G. J. Mulder.

[Continued from p. 346]

Analysis of Bile not perfectly fresh.—The bile of six animals, three to seven days old, was in winter evaporated to dryness, exhausted with absolute alcohol, and the alcoholic solution decolorized with animal charcoal; this was exhausted with muriatic acid, washed with water and exhausted with alcohol, the alcoholic solution almost evaporated to dryness, and æther poured upon the remaining colourless mass. On the next day, the temperature of the air not being very low, the whole had become converted into acicular crystals*. The crystallized mass was now repeatedly exhausted with æther, dissolved in water, and precipitated by neutral acetate of lead; a copious precipitate was formed; this was collected and washed with cold water. It was dried in a current of air at 248° F. It lost a large quantity of water when heated beyond 212° F. It was almost

* In fresh bile, treated in this way, a portion constantly remains uncrystallized, sometimes also in old bile; this consists of unmetamorphosed biline. If the whole crystallizes, the biline is completely decomposed, and the substance no longer possesses the nature of fresh bile.

perfectly white, but must contain some chloride, sulphate and phosphate of lead, although in small quantity.

After the liquid, which no longer yielded a precipitate with the neutral acetate, was filtered from the precipitate, it was treated with basic acetate of lead, but in such quantity that the liquid remained acid, to prevent the influence of the carbonic acid of the air. A copious perfectly white precipitate was formed, which was separated by filtration and washed with water. This second lead-salt was also very difficult to dry, and could only be obtained in the dry state by desiccation as above at 266° F.

The first lead-salt was incinerated so as to oxidize the lead; the oxide contained an admixture of sulphate and phosphate. On ultimate analysis, deducting the inorganic constituents, it yielded—

	I.	II.
Carbon	65·35	65·96
Hydrogen	8·71	8·84
Nitrogen	3·82	3·82
Sulphur and oxygen	22·12	21·38

The second lead-salt yielded—

	I.	II.
Carbon	66·44	67·01
Hydrogen	9·14	9·20
Nitrogen	3·66	3·66
Oxygen and sulphur	20·76	20·13

The second lead-salt, which as regards the organic matter may be considered as pure, thus yields results which differ considerably from all other analyses of the so-called choleic acid which have been made. The first lead-salt is not pure; the determination of the lead must be incorrect, from the volatilization of the chloride as well as the admixture of sulphate and phosphate.

Further experiments were then made upon the lead-salts obtained from bile, which had been kept several days, but never more than twelve. The bile was evaporated to dryness in a water-bath, exhausted with alcohol (0·867), and then decolorized with animal charcoal. The solution could not be perfectly decolorized, as absolute alcohol was not used. When evaporated to the consistence of a thin syrup, it was exhausted with æther, then dissolved in dilute alcohol, and treated with excess of a solution of neutral acetate of lead in alcohol (0·867). The flaky, almost white precipitate was filtered after subsidence. The liquid could not be made perfectly clear by filtration, and had an amber-yellow colour. This *first lead-salt from alcohol* was but small in quantity. The fluid separated from it, and which was acid and contained excess of acetate of lead, was not rendered turbid by alcohol, but milk-white by water; the precipitate produced by water could not be collected on a filter. The liquid was treated with an aqueous solution of acetate of lead; a large quantity of a perfectly white precipitate was then thrown down with water; this was filtered off and washed with water. This fluid did not run through perfectly clear; it was acid. This *second salt, produced by*

acetate of lead and water, is perfectly soluble in alcohol. Basic acetate of lead was then added to the filtered fluid, when another copious and perfectly white precipitate was obtained; the basic acetate was only added as long as the liquid remained acid. The precipitate was washed with water. The amount of this *lead-salt* thrown down *by basic acetate of lead* was somewhat less than the last. The fluid filtered from it was then treated with ammonia in excess. It yielded a white precipitate amounting to about one-fourth of the last. This *fourth lead-salt*, produced *by means of basic acetate of lead and ammonia*, as also the precipitate by basic acetate of lead, were dried in the air, exhausted with alcohol, to separate basic acetate and carbonate of lead; the solutions were evaporated in a water-bath and analysed. The soda of the bile and the lead were then separated from the remaining fluid. Biline, taurine, glycerine (?) and extractive matter remained in the residue.

The method of preparing the lead-salt, which was obtained by precipitation *with neutral acetate of lead and water*, was now modified, and the precipitate first produced collected separately from the subsequent one. This was done to ascertain whether choleate of soda alone occurs in the pure bile or other substances also. It was thus evident that the statement of Berzelius, that the bile is not completely precipitated by basic acetate of lead, is perfectly correct; for after the precipitation with neutral acetate of lead, and basic acetate of lead and ammonia, a considerable quantity of a substance which would not combine with lead always remained in solution.

First Lead-salt from Alcohol.—As stated above, it was precipitated by an alcoholic solution of acetate of lead from the alcoholic solution of pure bile. This precipitate consisted of combinations of the fatty acids of the bile with oxide of lead and of chloride and sulphate of lead, and contained no other organic matter of the bile. This process serves to separate the impurities from the following compounds, so that they are obtained in a state of greater purity.

The *second salt, thrown down by acetate of lead and water*, must still contain traces of fatty salts. The following analyses were made with this substance, and the subsequent ones with that freed from these admixtures. It was completely soluble in alcohol.

It was dried at 266° F. for a long time. It yielded—

	I.		II.	
	a.	*b.*		
Carbon	67·78	67·65	67·65	67·60
Hydrogen	9·04	9·23	9·29	9·26
Nitrogen	..	..	3·42	3·42
Oxygen and sulphur	..	..	19·64	19·72

I. The oxide of lead obtained from this was mixed with sulphate and phosphate of lead.

II. This was from a different preparation.

The agreement of *a* with *b*, the first and lastly deposited matters, and of I. and II., prepared in a totally different way and with different kinds of bile, is perfect. They are not however perfectly

pure lead-salts, but contain fatty acids and other salts of lead; the above composition is therefore that of an impure substance.

The basic acetate of lead-salt, prepared as described above, was treated with alcohol, the solution evaporated, and the residue dried at 266° F. It yielded on analysis—

Carbon	66·28	66·66	66·36
Hydrogen	9·25	9·26	9·25
Nitrogen	2·89	3·39	3·39
Oxygen and sulphur	21·58	20·69	21·00

The salt precipitated by ammonia from the mother-liquor of the last salt was exhausted with alcohol, the solution evaporated, and the residue dried at 266° F. It yielded—

	a.	*b.*
Carbon	66·25	65·95
Hydrogen	9·41	9·31
Nitrogen	3·50	3·50
Oxygen and sulphur	20·83	21·24

And from another preparation—

Carbon	66·14
Hydrogen	9·39

These analyses of the salts, which must all be considered as impure, merely serve to show that the amount of carbon they contain, although too little must be obtained on account of the difficulty in drying, is nevertheless higher than in several former analyses.

The above salts must still contain biline mixed with fellinic and cholinic acids; for the bilifellinate, the bilicholinate and fellinate of lead are soluble in alcohol; but the cholate of lead is insoluble in it, and hence could not be contained in the salts.

The lead-salts were then purified in different ways, by solution in alcohol, filtration from the residue, separation of the organic matter by sulphuretted hydrogen, and exhaustion of the dried matter obtained on evaporation with æther, to remove the fatty acids. The acids were next dissolved in carbonate of soda, and treated with acetate of lead, the precipitate of carbonate of lead and the lead-salt of the bile dried, exhausted with absolute alcohol, the solution evaporated, and the residue dried at 266° F.

Subjected to this treatment, the *salt precipitated by acetate of lead and water* yielded—

			Calculated.
Carbon	67·36	102	67·31
Hydrogen	9·21	86	9·40
Nitrogen	2·85	2	3·08
Oxygen	18·91	21	18·45
Sulphur	1·67	1	1·76

The precipitate obtained from the aqueous solution by neutral acetate of lead (p. 382), treated in the same way, carbonate of ammonia being used instead of the soda, the fats being removed by æther, yielded 19·32 per cent. of oxide of lead.

The impure lead-salt (p. 382), treated in the same way with the

carbonate of soda and without the lead, gave a soda-salt, which dried at 266° F. yielded 6·7 per cent. of soda. The latter result agrees perfectly with that of Theyer and Schlosser; but the salt is obviously impure, containing carbonate of soda. It is therefore unfit for analysis.

On the further analysis of the above salts of lead, it was found that in all the pure salts the organic matter was the same; and that, according as the soda-salts were precipitated by the neutral acetate, the basic acetate of lead or the neutral acetate and ammonia, precipitates were produced which contained 1–1½ or 2 equivs. of oxide of lead.

The quantity of soda, 6·53–6·68 per cent., which is, according to Theyer and Schlosser, contained in the bile in combination with the so-called choleic acid, is much too great; Mulder estimates it at 5·45 per cent., calculating it from the oxide of lead in the lead-salt yielding 19·51 per cent. According to him, the excess must arise from the presence of carbonate of soda, as had been previously shown by Gmelin. Moreover, the 6·30–6·95 per cent. of soda in the artificially-prepared choleate of soda must be too much, in consequence of the admixture of inorganic soda-salts. Again, the soda is only partly combined with choleic acid, because the biline is itself indifferent, and only yields this acid as a product of decomposition. Moreover, that portion which is not precipitated from the bile by acetate of lead is uncombined with soda. The author found a considerable quantity of alkaline carbonate in fresh bile, which is absent in the stale fluid. By dissolving the lead-salts several times in hot alcohol, a portion of bilicholinate and cholinate of lead was separable; and thus, if this is not done, the lead-salts of the so-called choleic acid are contaminated with it.

To determine whether the so-called choleic acid, as Berzelius thinks, was a mixture of bilifellinic and bilicholinic acids with dyslysine, Mulder examined the organic substance in the lead-salts. According to his view, dyslysine may exist in this mixture when the bile has been treated with strong acids; but if it has been precipitated at once with salts of lead, it is not necessarily present. The lead-salts of bile not perfectly fresh, which were perfectly soluble in alcohol, were digested with excess of oxide of lead and water in the water-bath. The former were partially dissolved by the latter; for the fluid, when poured off, became turbid on cooling, and was copiously precipitated by sulphuretted hydrogen. When no more was dissolved, the solution was filtered and evaporated, and left a somewhat sweet, but very slightly bitter extract, which possessed totally different properties from those of the substance in the lead-salt, and consisted of biline, *i. e.* that portion which is not precipitated from bile by subacetate of lead; it was converted by muriatic acid with heat into dyslysine, taurine and muriate of ammonia.

The salt containing the excess of oxide of lead was next boiled with alcohol, and the solution filtered and evaporated. A precipitate of carbonate of lead subsided. Sulphuretted hydrogen was then passed through the fluid, which was filtered; the clear solution eva-

porated to dryness, and the dry residue exhausted with alcohol; taurine then remained. The alcoholic fluid was then again evaporated to dryness, and the residue mixed with barytic water; a copious precipitate fell. This was separated by filtration.

This precipitate was almost entirely soluble in alcohol, and therefore consisted of fellinate of baryta. The insoluble portion, when freed from carbonate of baryta by muriatic acid, yielded a trace of cholinic acid.

Thus, by the digestion of that organic matter which was originally perfectly soluble in barytic water, with oxide of lead, biline and taurine were evolved; and after the separation of the biline and taurine, a considerable portion of the organic matter was insoluble in barytic water. A more perfect proof of the presence of biline with fellinic acid in the organic matter of the lead-salt, and hence of the compound nature of the so-called choleic acid, could not be produced. The taurine did not originally exist in it, but was a product of decomposition of a portion of the biline under the influence of the oxide of lead; moreover, the substance which was previously combined with oxide of lead and soluble in barytic water, was now separated into free biline, taurine, fellinic and cholinic acids, all of which bodies are also present in the freshest bile. The portion which remained dissolved in the barytic water proved this on analysis. When dried at 266° F., it yielded—

Baryta.....	13·93	13·85
Bilifellinic acid	86·07	86·15

and on combustion, carbon, 65·25; hydrogen, 9·22.

The organic matter in the lead-salts was now separated, and purified by treatment with barytic water. This caused the separation of sulphuric, phosphoric and the fatty acids, because their salts are insoluble in barytic water; and, for the same reason, fellinic and cholinic acids are also separated. The barytic compound contained 14·22 per cent. of baryta; this gives the same atomic weight, or nearly so, as that deduced from the pure lead-salt. Organic analysis, in conjunction with the determination of the baryta, yielded—

			Calculated.
Carbon.....	66·83	102	67·31
Hydrogen.....	9·33	86	9·40
Nitrogen	3·00	2	3·08
Oxygen.....	19·25	21	18·45
Sulphur.....	1·59	1	1·76

It contains the elements of $4C^{50}H^{39}O^{9}$ + 1 equiv. of taurine and 3 of ammonia. The substance, when treated with muriatic acid, yields only dyslysine, taurine and ammonia; its composition may therefore be expressed as above. It is called *bilifellinic acid*, with a minimum of biline, and is the same as that in the above lead-salts; it could not differ very materially from it, because on treatment with barytic water but little foreign matter was separated. To obtain this bilifellinic acid pure, bile kept from four to six days (in winter) is evaporated to dryness, exhausted with alcohol, decolorized with

animal charcoal, evaporated, the residue exhausted with æther, dissolved in alcohol, and precipitated with a spirituous solution of acetate of lead, the precipitate separated by filtration, water, basic acetate of lead and ammonia are then added, and the precipitate washed with water. This precipitate is exhausted with alcohol, sulphuretted hydrogen passed through the solution, which is filtered and evaporated, the residue mixed cold with barytic water, filtered, carbonic acid passed into the solution, which is heated, again filtered and evaporated, or the baryta precipitated by sulphuric acid.

The bile is however by no means a soda-salt of bilifellinic acid; but it also contains a very important constituent besides the small quantities of the products of decomposition mixed with it. It is evident from the above investigation,—1st, that in bile which is not perfectly fresh, after having been decolorized by animal charcoal, *bilifellinic acid* with a minimum of biline, $C^{102} H^{86} N^2 O^{21} S$, is present; 2nd, that in the bile this acid is always mixed with fellinic and cholinic acids, which, if they are not separated by baryta, render all the salts impure; 3rd, that except the substance mentioned in 1 and 2, in bile which has been evaporated to dryness, decolorized with animal charcoal, and exhausted with æther, we do not find many substances which are retained by the charcoal and dissolved by the æther; we obtain but one principal substance, bilifellinic acid; 4th, that the portion of the bile which is known as *biline*, and is not precipitable by basic acetate of lead and ammonia, contains very important constituents; its quantity is much less in stale than in fresh bile, and may be converted into that product of decomposition of the bile which exists in the lead-salts.

Perfectly Fresh Bile.—This cannot be completely precipitated by basic acetate of lead, but leaves a considerable quantity of matter in solution. That constituent, which is capable of combining with oxide of lead, yields when dried the same products of decomposition as biline with muriatic acid. The examination of the fresh bile was effected in the same way as that detailed above, *i. e.* by treatment with acetate of lead. The author, from his investigations, which are carried out to the most minute detail, and which we cannot fully enter into, and the most important points of which we have given above, arrives at the conclusion, that the fresh bile contains a large quantity of biline, which is partly free, partly combined as fellinic and cholinic acids, and which also yields these acids, as well as taurine and ammonia, as products of decomposition; so that by this investigation also the statement that biline must contain the elements of NH^3, $C^4 H^7 NO^6 S^2$ and $C^{50} H^{36} O^6 + n$ aq is confirmed.—Abstracted from *Untersuchungen über die Galle*, Frankfurt a. M. 1847.

On the Relations of Glycocoll and Alcargene. By T. S. Hunt.

The similarity which exists between the compounds of nitrogen and arsenic is such, that they are regarded as belonging to the same natural group, and capable of replacing each other in combination. Cacodyle and its derivatives are as yet the only organic bodies

known which contain arsenic; of these M. Gerhardt has shown that alcarsine is to be regarded as an alkaloid in which arsenic takes the place of nitrogen, but the parallel substance containing nitrogen is as yet unknown; and hitherto we have been unable to complete the analogy between these elements, by the discovery of two corresponding compounds, the one containing nitrogen and the other arsenic.

The substance known as glycocoll or gelatine-sugar is shown by the recent researches of Horsford and Laurent, to have the composition before suggested by Gerhardt and declared by Dessaignes from the results of the decomposition of hippuric acid. Its equivalent is represented by the formula $C^4 H^5 NO^4$. The alcargene or cacodylic acid of M. Bunsen is produced by the slow oxidation of cacodyle or alcarsine; 1 equiv. of alcarsine and 8 of oxygen yield 2 of alcargene and 2 of water*,

$$C^8 H^{12} As^2 O^2 + 8O = 2C^4 H^5 AsO^4 + 2HO.$$

The equivalent of this substance then is represented by $C^4 H^5 AsO^4$, which differs from the formula of glycocoll only in the substitution of As for N.

A notice of some of the characters of the two substances will serve to show their close affinity. Both glycocoll and alcargene are capable of exchanging 1 equiv. of their hydrogen for a metal; and in addition to this character, in which they resemble acids, act the part of organic bases by combining directly with acids to form definite crystallizable compounds. Some of these corresponding combinations are here represented:—

Glycocoll..	$C^4 H^5 NO^4$	Alcargene..	$C^4 H^5 As O^4$
Argentic	$C^4 (H^4 Ag) NO^4$	Argentic	$C^4 (H^4 Ag) AsO^4$
Hydrochloric..	$C^4 H^5 NO^4, HCl$	Hydrochloric.	$C^4 H^5 AsO^4, HCl$

To these characters we may add, that both glycocoll and alcargene are readily soluble in water, sparingly soluble in alcohol, crystallize with facility, and are not volatile without decomposition. They also resemble each other in having no deleterious action upon the animal system, a property that is very remarkable in a body which like alcargene contains more than 72 per cent. of arsenic. From these facts the conclusion seems unavoidable, that alcargene is the arsenical species of a genus of which glycocoll may be regarded as the type.

Glycocoll is isomeric with the hyponitrous æther of Liebig. This substance, which is regarded by M. Gerhardt as the nitric species of acetene $C^4 H^6$, is, like many other bodies of a similar constitution, decomposed by the action of sulphuretted hydrogen. When a current of this gas is passed into an alcoholic solution of the æther, previously mixed with a little solution of ammonia, it is rapidly absorbed, while the liquid assumes a dark orange-red colour and deposits a large amount of sulphur. In this process a volatile substance of a powerful alliaceous odour and pungent taste is formed;

* See the corrected formula for this substance in M. Gerhardt's 'Précis de Chimie Organique,' vol. ii. p. 445.

but the small quantity which I obtained in a single experiment did not allow me to determine its nature. It may perhaps be a body corresponding to alcarsine, of the formula $C^8 H^{12} N^2 O^2$, or a sulphuretted species of it. 4 equivs. of the æther and 8 of the sulphuretted hydrogen would yield 1 equiv. of this compound with the separation of 6 equivs. of water and 8 of sulphur; the tendency of the bodies of the acetic series to unite and double their equivalent is well known. This however is merely a probable conjecture, and I shall take the earliest opportunity to determine its truth or falsity. The substance $C^8 H^{12} N^2 O^2$ should yield glycocoll by oxidizing agents.

It will be very important to examine the action of reducing agents and sulphuretted hydrogen upon glycocoll, as alcargene by these means affords alcarsine, and a species in which its oxygen is replaced by sulphur. I have commenced some researches upon these points, the results of which I will send you as soon as they are completed. —Silliman's *Journal*, Sept. 1847.

On Perchromic Acid. By M. Barreswil.

On mixing a concentrated solution of chromic acid with an equally concentrated solution of peroxide of hydrogen, a violent effervescence is immediately produced by an escape of pure oxygen; when, on the contrary, the solutions are mixed in a very diluted state, the liquid assumes an intense blue colour. This blue colour is of extremely slight stability, and appears to point to the formation of a very readily decomposable higher oxide of chromium than chromic acid; and which, when concentrated solutions are employed, is decomposed immediately on its production. The blue compound may be obtained by mixing a dilute solution of peroxide of barium with an excess of muriatic acid and a dilute solution of bichromate of potash, but it is so unstable that it cannot be isolated from this liquid. It is, however, according to the following experiments, perchromic acid, $Cr^2 O^7$. To determine the constituents of this body, the author made use of Gay-Lussac and Thenard's apparatus for the analysis of organic substances with chlorate of potash, substituting for the tube a balloon capable of holding half a pint of water. The balloon was half-filled with impure very acid peroxide of hydrogen, and placed in cold water. A tube connected with the balloon passed with its curved end under a graduated cylinder entirely filled with water. The apparatus so arranged was left for twenty-four hours, during which time not a bubble of gas passed into the cylinder. Upon this an accurately weighed quantity of bichromate of potash, in pieces of a nearly equal size, was conveyed through the cock into the liquid. As these pieces fell into the liquid they were surrounded with blue streaks, and bubbles of gas were disengaged, which passed into the cylinder. When the whole of the bichromate of potash had been added to the liquid, the amount of gas disengaged was read off after two hours' standing, and a second reading made after twenty-four hours; during this interval there was no perceptible increase of gas,

although the liquid still contained peroxide of hydrogen. The chromium is no longer contained in the liquid as chromic acid when the evolution of oxygen has ceased, for the acid itself loses a portion of its oxygen during the effervescence, and is left as oxide. 0·5 grm. bichromate of potash disengaged,—I. 152, II. 157, III. 150, IV. 151, V. 150 cubic centimetres of oxygen, that is 1 equiv. of the salt to 4 equivs. of the latter, theory requiring 151 (equiv. of chromium = 310) or 155 (equiv. of chromium = 328). Now since the chromium in 1 equiv. of the bichromate of potash, after it has been converted into the blue compound, and this again decomposed, is left behind as oxide, and consequently 1 equiv. of the salt parts with 3 equivs. of its oxygen, we may thence conclude that the peroxide of hydrogen, for every equivalent of the salt, adds 1 equiv. of oxygen to 6 in the chromic acid of the salt, so that the blue body obtains the composition $Cr^2 O^7$. The reaction which gives rise to the perchromic acid may be expressed in the following manner:—

$$2(KO, CrO^3) + HCl + O = KCl + HO + Cr^2 O^7.$$

The decomposition of the perchromic acid in the muriatic liquid is

$$Cr^2 O^7 + 3HCl = Cr^2 Cl^3, 3HO + O^4.$$

It was attempted to confirm this reaction by the isolation of the perchromic acid; but all experiments to combine the blue body with an inorganic base failed, and after the experiment was concluded a chromate was constantly found in the liquid. Æther, on the contrary, by being agitated with the aqueous liquid, immediately took up the blue body, the water became colourless, and the supernatant æther blue. But as soon as the æther was removed and evaporated, the water dissolved in it was found to contain chromic acid, as in the preceding experiments, and not oxide of chromium. The author succeeded in combining perchromic acid with vegetable bases. Quinine and strychnine dissolved in æther were precipitated of a dirty violet by the perchromic acid, extracted with æther from the aqueous solution; but the stability of these salts was very slight, and they could only be kept a few hours after their preparation.

Some experiments to procure higher oxides of other metallic acids led, in the case of vanadic acid, to the following result:—On treating the vanadiate of ammonia in the same manner as the chromate of potash in the preceding experiments, the liquid assumed a blood-red colour, which was more constant; but from the small quantity of material at the author's disposal, the compound could not be further examined.—*Ann. de Chim. et de Phys.*, xx. p. 364.

ANALYTICAL CHEMISTRY.

On the Analysis of Gunpowder. *By* Prof. R. F. Marchand.

The following is an abstract of a very extensive treatise by the author on this subject. To *determine the amount of water*, a crucible

filled with the powder is suspended in a wide-necked closed bottle, covered at the bottom with concentrated sulphuric acid. The powder employed in all the following analyses (so-called Bernese sporting powder) lost 1·13–1·10 per cent. humidity.

Determination of the Nitre.—After having endeavoured to ascertain the amount of nitre by moistening the powder with sulphuric acid and subsequent ignition, or by mixing with sal-ammoniac, heating to redness, and converting the residue into sulphate, the author adopted the two following methods:—

I. *Extracting the Nitre with Water.*—The gunpowder, without being pulverized, is treated in a beaker with hot water, and frequently agitated; this operation is repeated, and the residue then brought upon a dried weighed filter, and most carefully washed. It is best to evaporate the filtered solution in a water-bath; the residuary nitre is fused. The residue collected on the filter is dried in the flask over sulphuric acid, and weighed after some days. In an experiment made according to this plan, the author obtained 79·06 per cent. nitre and 21·03 sulphur and charcoal. The operation of washing may be very much shortened by placing the powder in a displacement apparatus of the form of an ordinary chloride of calcium tube, from 7 to 8 inches long and three-quarters of an inch broad, the bulb of which is stopped with some asbestos, while the other end is closed by a cork, through which a tube 3 feet long passes, and which is filled with water.

The amount of nitre may also be ascertained by determining the nitrogen in the powder; a portion of the sample is weighed off, reduced to a fine powder, and intimately mixed with oxide of copper, and then filled into the combustion-tube, which is charged posteriorly with carbonate of lead, and then with oxide of copper; oxide of copper and metallic copper are placed in front of it. The author found by this method 79·2–79·3 per cent. nitre.

Estimation of the Sulphur.—This is best effected in the form of sulphate of baryta. A mixture of 1 part nitrate and 3 parts carbonate of baryta is intimately mixed with a twelfth part of gunpowder, and heated in a tube closed at one end. A layer, 3 to 4 inches in length, of the barytic salts is inserted in front of the mixture, and the whole is heated in the combustion-furnace, beginning at the anterior portion. The mixture does not fuse, and is easily removed from the tube, which is rinsed with dilute muriatic acid, and the ignited mass then dissolved in this. The liquid is retained in a beaker for several hours near 212°, upon which the sulphate of baryta is collected on a filter. The dry powder yielded 9·82 per cent. sulphur; however, as the sand in the powder (0·5 per cent.) is calculated as sulphate of baryta, the amount of sulphur is rather too high. Gay-Lussac's method is quite similar to this; but as the combustion is effected in a crucible, a slight loss is unavoidable. The powder is intimately mixed with the same quantity of nitre, carbonate of soda, and 4 times the quantity of common salt. The mixture is burnt white in a platinum crucible. A small quantity of sand is left on dissolving the fused mass in muriatic acid. The dry

gunpowder yielded, according to this method, 9·52 per cent. sulphur. As some sulphur escaped unburnt, the operation was made in a glass tube, when 9·76 per cent. sulphur were obtained.

The amount of sulphur may likewise be determined with certainty in the moist way. From 2 to 3 grms. of the powder are treated in a glass flask with concentrated nitric acid, and the addition of about 1–2 decigrms. chlorate of potash; the mass is kept gently boiling; from time to time the same quantity of chlorate of potash is added, until at last a colourless liquid is obtained, which is diluted with a large quantity of water, and precipitated while hot with chloride of barium; in this way the author found for the dry powder 9·72 and 9·84 per cent. sulphur. If the reaction is effected in a retort, a small quantity of sulphuric acid may be found in the distilled liquid (6 milligrms.) sulphate of baryta for 5 grms. powder; it is therefore advisable to conduct the distillation in a tubulated retort, and to mix the distillate with the contents of the retort.

Separation of the Sulphur from the Charcoal.—Wöhler's method may be employed for this purpose, *i. e.* an indefinite quantity of the mixture of sulphur and charcoal, as dry as possible, is brought into the bulb of a weighed reduction-tube; the tube is filled with metallic copper; it is heated in a current of dry hydrogen gas, which drives the sulphur into the copper; the tube is then weighed, and likewise after shaking out the residuary charcoal. In this way the relative quantity of sulphur and charcoal is obtained. The heat which must be applied to remove the whole of the sulphur from the charcoal is in general greater than that at which the charcoal had been prepared; and there is generally observed, during the expulsion of the sulphur, a strong odour of humic acid, carbonic acid, carbonic oxide and water. The author found, according to this method, with a long-continued but faint ignition, for 100 parts sulphur 119 parts charcoal; but this is certainly too little. When heated strongly over a Berzelius's lamp, there were 109 parts charcoal for 100 parts sulphur.

Instead of distilling the sulphur from the charcoal, it may also be removed by solvents. The author employed for this purpose sulphuret of carbon. After exhausting the gunpowder with water in the extracting tube, it is treated with absolute alcohol, which displaces the water, upon which sulphuret of carbon, which has been rectified over oxide of lead, is poured over it until what passes through leaves no sulphur on evaporation; the powder is then finally treated with alcohol. It is still better to use the sulphuret of carbon mixed with absolute alcohol.

As soon as the charcoal is washed, a current of dry air is drawn through the tube by means of an aspirator, the tube itself being confined in an air-bath at 248°. The dry charcoal is weighed accurately in the tube. One experiment yielded 10·99 per cent. charcoal; there is however a slight loss here, as the water with which the charcoal is washed does not pass through colourless. When alcohol is boiled with slightly-burnt charcoal, the liquid becomes turbid on cooling, and deposits white flakes on the addition of water.

The sand, &c. contained in the powder may be approximatively determined by trituration and suspension. 100 grms. of gunpowder yielded by this method 0·148 grm. sand, a number which must be somewhat too small. When the charcoal is burnt, after extracting the nitre and distilling off the sulphur, a pretty considerable quantity of ash is obtained, which includes the sand and the impurities of the sulphur. 2·3 grms. charcoal (or 21 grms. gunpowder) left a residue of 0·120 grm.; of this about 0·020 grm. ash must be referred to the charcoal and 0·030 to sand, so that the sulphur must have contained 0·070 impurity, or above 3 per cent. This certainly is too much, and most of it must be calculated as sand. The mean of all the analyses is—

Nitre	79·16
Sulphur	9·72
Charcoal	10·99
	99·87

The nitre which is obtained should be tested with nitrate of silver as to the presence of chlorine, and the sulphur as to arsenic, by washing with ammonia and the addition of an acid. It is also important to determine the composition of the charcoal. The mixture of sulphur and charcoal obtained by exhaustion with water is burnt in a current of oxygen or with chromate of potash, and the water and carbonic acid weighed. A tube containing peroxide of lead should be inserted between the chloride of calcium tube and the potash apparatus, in order to absorb the sulphurous acid. The charcoal of the gunpowder examined contained 88·52 carbon and 2·40 per cent. hydrogen after deducting the ash.—*Journ. für Prakt. Chem.*, xxxviii. p. 193.

On a Method of separating Sulphurous Acid from Carbonic Acid. *By* J. Persoz.

In the year 1838 the author described a method of converting, by means of a saturated solution of iodate of potash, sulphurous acid when mixed with carbonic acid into sulphuric acid, and of removing it in this manner from the mixture. On employing this method to find the volume of the sulphurous acid, the residuary volume of carbonic acid must be subtracted; and further, since the solution of the iodate of potash absorbs an equal volume of carbonic acid, the volume of this solution must also be subtracted from that of the mixture of the two acids. Instead of the solution of the iodate of potash, a glass rod, covered with paste and coated with powdered iodate of potash or soda, may be introduced into the graduated tube containing the mixture of the two gases. As soon as no further decrease in the quantity of the confined gas is perceptible, the glass rod is removed and the gas measured at once. Before considering the carbonic acid as freed from sulphurous acid, another glass rod should be introduced, which is coated with the paste made

with starch and a dilute solution of iodate of potash; if the least trace of sulphurous acid is contained in the gas, it is instantly coloured blue. This method can also be used to detect minute traces of sulphurous acid.—*Ann. de Chim. et de Phys.*, lxx. p. 254.

CHEMICAL PREPARATIONS.

On the Preparation of the Iodide of Lead. By M. Boudet.

When iodide of lead is prepared by precipitating acetate of lead by iodide of potassium, a certain quantity of iodide of lead always remains dissolved in the liquid. Lepaire, who long since drew attention to the fact, states that this remainder of iodide of lead may be precipitated by the addition of a few drops of nitric acid, while basic acetate of lead sends down tribasic iodide of lead, and sulphuric and muriatic acids liberate iodine. On evaporating the liquid, it leaves, according to Lepaire, a white residue, which on treatment with water again deposits protiodide of lead. The experiments made by the author on this subject confirm the previous statements. In order to discover whether the acetate of potash, which is formed by the double decomposition, is the cause of the increased solubility of the iodide of lead, the author triturated iodide of lead together with some acetate of potash. The mixture, after having deliquesced to a syrup from the absorption of moisture, soon became perfectly white, and had no reaction upon blue litmus-paper. After some length of time, silky needles of the protiodide of lead and potassium separated; on adding water to the mixture, the yellow iodide of lead was precipitated, and the liquid became acid. This liquid subsequently afforded with basic acetate of lead a yellow precipitate, and nitric acid and very dilute sulphuric acid likewise threw down some yellow iodide of lead. When the white syrupy mixture of acetate of potash and iodide of lead was previously extracted with alcohol, the white residue deposited, on the addition of a weak acid, a yellow protiodide of lead, and the filtered liquid gave, on the addition of nitric acid, a precipitate of the same compound. When, on the other hand, iodide of lead was boiled with an aqueous solution of acetate of potash, the author obtained a colourless acid liquid, which deposited white silky crystals of the protiodide of lead and potassium, while an insoluble yellowish-white residue of the oxyiodide of lead was left. Hence it appears that wherever acetate of potash and iodide of lead come in contact with each other, the precipitate never contains the whole of the iodide of lead formed; but, on the contrary, there is always a loss due to the protiodide of lead and potassium remaining in solution. No such loss occurs on precipitating iodide of potassium with nitrate of lead.—*Journ. de Pharm. et de Chim.*, xi. p. 274.

On the Removal of the Bitter Taste of Sulphate of Magnesia. *By* M. Combes.

It has long been a desideratum to remove the bitter taste of that valuable purgative salt the sulphate of magnesia. After a number of trials, I have at last succeeded in effecting this by the simultaneous administration of tannine or coffee; the former however is the active agent. 1½ gr. of tannine, when boiled for 3 minutes with an ounce of the sulphate and about 1½ pint of water, entirely conceals the taste of the salt. The peculiar astringent taste of the tannine may be removed by an agreeable aroma. In roasted coffee we have both the advantages combined. The following are the best proportions:—Take of

Sulphate of magnesia, 1 oz.
Powder of roasted coffee, 2½ drms.
Water, about 16 oz.

Boil well for two minutes (not in a tinned vessel), remove from the fire, and let the mixture infuse for some minutes, so as to allow time for the development of the aroma; then filter, or merely strain off. It must be sweetened to taste. This fluid does not impart the slightest taste of the bitterness of the sulphate. The salt does not undergo any decomposition by this process.

It should be observed that the infusion is not capable of removing the bitterness, nor will the addition of the salt to the filtered decoction answer the purpose.

Should it be required to increase the amount of the sulphate without augmenting the proportion of coffee, 2 or 3 grs. of tannine should be added to the boiling decoction. The aroma of the coffee masks the disagreeable taste of the tannine. Orange-flower water is also useful in concealing the flavour of tannine.—*Journ. de Pharm.*, August 1847.

On the Preparation of pure and Carbonated Oxide of Zinc. *By* M. Lefort.

To avoid the presence of alkali in the oxide of zinc prepared in the moist way, Defferre proposed precipitating the chloride with caustic ammonia; but in this manner, as Guibourt has shown, a mixture of ammoniacal oxychloride and hydrated oxide of zinc is obtained. The best method therefore of preparing oxide of zinc is still by means of the alkaline carbonates. When equivalents of carbonate of potash or soda and a soluble salt of zinc are mixed together at the ordinary temperature, a voluminous precipitate is obtained, which parts with three-fourths of its weight of water over sulphuric acid, and forms a frequently impure carbonate of zinc, which is difficult to pulverize. When, on the contrary, boiling solutions are employed, a white salt of homogeneous composition is obtained, which is easily washed, and leaves on ignition readily-pulverizable oxide. When the salt is perfectly dried and then heated, it begins to part with water between 230° and 294°, and only disengages carbonic acid at 572°. The author obtained on analysis 72·73–73·11

per cent. ZcO and 14·64–14·30 per cent. CO^2, which agrees with the formula $3CO^2, 8ZcO + 6HO$, advanced by Berzelius.

When cold solutions of bicarbonate of potash or soda are mixed with a soluble salt of zinc, a white precipitate is gradually formed, with disengagement of carbonic acid, which, washed and dried over sulphuric acid, presents the greatest resemblance to *magnesia alba*. When boiling solutions are used, the preceding salt, $3CO^2 8ZcO + 6HO$, is obtained. The precipitate obtained from the cold solution begins to part with its water at 212° and its carbonic acid at 500°. Analysis yielded 61·94–61·93 ZcO and 11·00–11·31 per cent. CO^2. The formula for this salt is therefore $CO^2 3ZcO + 6HO$. Smithson examined a native carbonate of zinc, which had the formula $CO^2, 3ZcO + 3HO$, containing therefore only 3 equivs. water less than the artificial.—*Journ. de Pharm. et de Chim.*, xi. p. 329.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Process of M. Armand Rousseau, *for producing upon Porcelain a fine Dead Silver, not affected by Sulphureous Exhalations. By* M. Alexander Brongniart.

M. Armand Rousseau, decorator of porcelain, presented to the Society for the Encouragement of Arts, Paris, specimens of porcelain, the principal decoration of which consists of wavy lines, having the appearance of dead silver. This dead silver, which is of a fine white colour, being relieved by ornaments of blue or any other lively colour, produces a very good effect, and presents the appearance at first sight of white mother-of-pearl, or that which reflects no prismatic colours.

This application of silver on porcelain was well known before M. Rousseau's process; but the results were in general imperfect, being less pure and possessing less metal than the specimens submitted to the Society. The dead silver prepared and applied by M. Rousseau admits of a very fine burnish being applied, the ground presenting the appearance of white pearl, which sets off to great advantage the ornaments painted thereon. The new process possesses however another advantage, of much greater importance than the above-mentioned improvements. It is well known, that by the action of air, charged with the most minute portion of sulphureous particles, silver loses, first its lustre, then its metallic appearance, and finally assumes a leaden appearance, approaching to black; this serious defect has caused the use of metallic silver to be rejected by all manufacturers who wish their porcelain to be ornamented in a durable and brilliant manner. The lustre may be renewed by cleansing; but the fine dead appearance of the silver, and also the burnishing, are quite destroyed; the brilliancy of the surrounding colours is deteriorated, and the friction, however carefully the cleansing may be effected, carries off a portion of the metal, which is necessarily laid on very thin.

By M. Rousseau's very simple process, the silver is completely protected from the injurious action of the sulphur, in whatever quantity and in whatever state it may be. This statement is proved by various facts. The Ceramic Museum at Sèvres has possessed, since the year 1845, specimens which were placed there by M. Rousseau at that time; and at the end of eighteen months they did not appear to have undergone any change. As it was not evident, however, that they had been exposed to any sulphureous exhalations while there, I requested M. Rousseau to furnish me with an article for the purpose of submitting it to the action of sulphuretted hydrogen gas; and he gave me the half of the tube of an opera-glass, which had been in use; this was exposed during several weeks in the chemical laboratory, and the only alteration it underwent was that it was turned slightly yellow; but this was easily removed by a little soap and water. Shortly afterwards the same piece was, together with the pretty little box now presented to the Society, fully exposed to the exhalations from a cesspool, which was being emptied; and they were both, when taken out, in their present state of freshness. From this it became evident that M. Rousseau was in possession of the secret of giving to dead silver (which is much more easily affected by vapours than burnished silver) the power of resisting the deleterious action of the strongest hydrosulphuric exhalations.

This important object is effected by the employment of gold. A very thin layer of this metal is laid, by means of a brush, over the silver with which the porcelain is ornamented, before firing it, when, by the help of a flux and a cherry-red heat, the two metals are fixed on the porcelain.

This is the principle, and the mode of putting it in practice; but its success depends upon the skill and experience of the operator. For instance, the silver must be dissolved in very dilute acid, and slowly precipitated, and the metallic precipitate must be well washed. The silver is then laid upon the porcelain before being coloured (or, if coloured, the colour must not be any preparation of gold), in a pasty state, and left for twenty-four hours, at the expiration of which time the gold is to be laid on, and the article fired at a moderate heat.—*Bulletin de la Société d'Encouragement*; as inserted in Newton's *Journal*.

On the Preparation of the Oxide of Chromium. By M. Barian.

The author mixes 4 parts of bichromate of potash with 1 part starch, and heats the mixture to redness in a crucible; then removes the carbonate of potash by washing, and heats again to redness. The oxide of chromium is so pure, that it may be employed in glass and porcelain painting, if the chromate of potash used was free from sulphate; this is easily ascertained by boiling a sample of the bichromate with 3 parts of tartaric acid, and when the evolution of carbonic acid has ceased, testing with chloride of barium and muriatic acid for sulphuric acid.—*Revue Scientif. et Indust.*, vol. xx. p. 425.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on the new Metal Ilmenium. By R. Hermann.

In the present treatise the author points out the difference between ilmenium and the new metal pelopium, discovered by Rose. In a previous notice*, the latter chemist drew a comparison between the properties of these two metals as far as was possible with the facts then known, and which showed that some differences existed in their behaviour. Rose placed pelopium between niobium and tantalium. According to Hermann, ilmenium forms with respect to tantalium the other extreme in this series of metals, resembling one another so much in a chemical point of view. The solution of the pelopate of soda, like that of the tantalate, is dissolved by muriatic acid to an opalescent liquid. Ilmenic acid is thrown down far more perfectly from the soda salt by muriatic acid than niobic acid; but the chloride of ilmenium dissolves when treated with concentrated muriatic acid without any turbidness in water. Zinc immediately colours this solution brown; and when the acid is neutralized by the zinc, brown flakes of oxide of ilmenium are precipitated; even the very dilute solution of ilmenic acid, which is sometimes obtained on precipitating the ilmenate of soda, is coloured brown by zinc. The solution of pelopic acid in muriatic acid, obtained by supersaturating the pelopate of soda, is not turned blue by zinc according to Rose; the pelopic acid merely acquires a somewhat less pure colour and becomes gray; it resembles therefore tantalic acid in its behaviour. Only after the addition of sulphuric acid does the acid become coloured, at first of a beautiful blue, and subsequently of a dirty blue, but not brown. Sulphuric acid poured over the chloride of pelopium, and subsequent addition of water, produces the blue most beautifully in contact with zinc. The solution of the chloride of pelopium in muriatic acid likewise gives rise to the blue colour, when it is diluted with water and zinc placed in the solution. Ilmenic acid, under similar circumstances, is coloured brown; it is consequently the only substance bearing a resemblance to tantalium, which is immediately coloured brown by zinc, without first being coloured blue.

The solution of the ilmenate of soda yields with tincture of galls

* Chem. Gaz., vol. iv. p. 451.

a dark brown precipitate when a large excess of alkali is present. A brighter precipitate is formed of a purplish-brown in the solution of the crystallized ilmenate of soda; while, according to Rose, pelopic acid yields an orange, tantalic acid a light yellow, and niobic acid a dark orange-red precipitate. Ferrocyanide of potassium precipitates the solution of the ilmenate of soda in muriatic acid with the brown colour of the hydrated peroxide of iron; the tantalate of soda, on the contrary, yields a sulphur-coloured precipitate; the niobate, according to Rose, a red; and the pelopate of soda, a brownish-red one. When ilmenic acid is ignited in a current of hydrogen, it immediately acquires a leaden hue; under the same conditions, pelopic and niobic acids immediately become black, according to Rose; tantalic acid does not change its colour. Before the blowpipe, ilmenic acid gives with borax and microcosmic salt, both in the outer and inner flame, colourless beads; and only when more is added than the flux is capable of dissolving, does the ilmenic acid acquire in the reduction-flame the same gray colour as on ignition in hydrogen; niobic acid gives with microcosmic salt in the inner flame a blue, pelopic acid a brown bead. 100 parts of ilmenic acid expel, on ignition with equal parts of carbonate of soda, 27·10–29·05 parts carbonic acid; a quantity which differs considerably from that found by Rose for pelopic acid, and which at the same time shows that ilmenic acid has a very different atomic weight to that of pelopic acid. The specific gravity of ilmenic acid, which is 4·1–4·35, likewise differs from that of pelopic acid. The distinguishing characters of ilmenic acid from pelopic acid are sufficiently evident; and considering the low atomic weight of ilmenic acid in comparison with those of the other substances bearing resemblance to tantalium, the difference will appear still greater when the combinations of pelopic acid are better known.

Besides yttroilmenite, ilmenic acid likewise occurs in the pyrochlor of Miask, of which it forms the chief constituent. But yttroilmenite is always so contaminated with columbite, that it is impossible to obtain one mineral perfectly free from the other; and consequently the acid prepared from it always contains niobic and pelopic acids, and, according to whether the former or latter predominates, colours the bead of microcosmic salt blue or brown. In order to separate the ilmenic acid from these impurities, the following process is adopted:—The yttroilmenite is reduced to a fine powder, and this fused with 6 times its weight of the bisulphate of potash; the fused mass is poured out, rubbed to a powder, and exhausted so long upon the filter with hot water as anything is removed; an impure ilmenic acid, containing sulphuric acid, is left upon the filter. If any tungstic acid had been found by preliminary experiment, the residue is digested with sulphuret of ammonium, and again well washed. After this treatment, the still moist ilmenic acid is evaporated to dryness with a sufficiently large quantity of the bisulphate of ammonia, and finally fused with it to a clear mass. On treating this fused mass with cold water, the whole of the ilmenic acid is deposited in transparent flakes. This precipitate is well washed, formed

into a thin paste with water, sulphuric acid added to it, and then evaporated until the excess of sulphuric acid begins to be expelled. The acid residue is mixed with a little water, poured upon a filter, and washed with water as long as the liquid which passes off has an acid taste. A combination of ilmenic with sulphuric acid remains on the filter, which usually no longer colours microcosmic salt; should this not be the case, the fusion with bisulphate of ammonia and evaporation with sulphuric acid is repeated until it is perfectly free from every admixture, when it is heated to redness to expel the sulphuric acid. The ilmenic acid may be prepared in the same manner from the pyrochlor of Miask. The acid employed for the following experiments was obtained from yttroilmenite.

Atomic Weight of Ilmenium.—100 parts of the chloride of ilmenium were decomposed with water and ammonia; the ilmenic acid was collected on a filter and ignited, and the liquid acidified with nitric acid precipitated with nitrate of silver; 1349·6 was adopted as the equivalent of silver, and 443·28 for that of chlorine. Calculating with these numbers, there were found 53·00 per cent. chlorine and 58·87 ilmenic acid; assuming the chloride of ilmenium to contain 1 equiv. metal to 2 of chlorine, this gives 786·18 as the equivalent of ilmenium according to the amount of chlorine found, and 790·70 from that of the ilmenic acid. Crystallized ilmenate of soda was deprived of water by ignition, rubbed to a fine powder, and a weighed quantity decomposed by fusion with bisulphate of ammonia. On dissolving the mass in water, ilmenic acid containing sulphuric acid was left, which was deprived of the sulphuric acid by a strong red heat. 100 parts of dry ilmenate of soda yielded 71·607 ilmenic acid and 28·393 soda. Adopting 389·729 as the equivalent of soda, 1 atom of ilmenic acid weighs 982·90, and 1 atom of ilmenium 782·90. The mean from the above experiments yields 786·59 as the equivalent of ilmenium.

Ilmenium and Oxide of Ilmenium.—The metal is obtained by igniting the combination of chloride of ilmenium with ammonia in an atmosphere of ammonia. It forms a porous black mass, resembling charred sugar; it acquires a lustre near the sides of the glass tube in which it had been prepared and under the polishing steel. The colour remains black. It is not dissolved or oxidized even on boiling by sulphuric, hydrochloric, nitric or hydrofluoric acid, and does not decompose water. It is readily dissolved by a mixture of hydrofluoric and nitric acids. When heated in the air, it burns to white ilmenic acid. The author regards the brown flakes which zinc precipitates from the muriatic solution of the chloride of ilmenium as oxide of ilmenium; when exposed to the air, it absorbs oxygen, and is converted into white ilmenic acid.

Ilmenate of the Oxide of Ilmenium and Ilmenic Acid.—When ilmenic acid is heated to redness in a current of hydrogen, it becomes bluish-gray, but loses little in weight. Hydrated ilmenic acid, and the combination with sulphuric acid, likewise experience a similar alteration of colour when they are moistened with hydrochloric acid and exposed to the action of zinc. The author regards this sub-

stance as a combination of ilmenic acid with oxide of ilmenium, perhaps $Il^2O^3 + 3IlO^2$. Ilmenic acid is obtained,—1st, by burning ilmenium; 2nd, by igniting the hydrate; 3rd, by heating the combination of ilmenic and sulphuric acid to bright redness. The acid obtained by methods 1 and 2 forms white fragments with an earthy fracture; that prepared according to 3 is in solid fragments, with a conchoidal, sometimes dull, sometimes shining fracture. When heated to redness, ilmenic acid assumes a yellow colour, which again disappears on cooling; the intensity of this colour depends on the state of aggregation of the acid; an acid containing alkali is coloured more strongly than pure acid. The composition of ilmenic acid is IlO^2, for 100 parts of the chloride of ilmenium gave 58·87 ilmenic acid and 53·00 chlorine. They contain therefore 47·00 ilmenium, which on oxidation absorb 4·87 oxygen to form 58·87 ilmenic acid; hence we have—

Ilmenium	79·84	1 =	786·59	79·72
Oxygen	20·16	2	200·00	20·28

Hydrated Ilmenic Acid is obtained by precipitating an alkaline ilmenate with an excess of hydrochloric acid, as well as by mixing chloride of ilmenium with water, or by very long-continued edulcoration of the sulphated ilmenic acid with water. In all these cases it resembles in appearance recently-precipitated alumina. That prepared according to the first method still retains a considerable quantity of alkali. The hydrate precipitated with muriatic acid from the ilmenate of soda and dried at 212° contained 24·23 per cent. water. On continued desiccation over sulphuric acid at a low temperature, it continually lost water, and contained after a long time 16·20 per cent., which quantity does not correspond with any definite composition.

Sulphuret of Ilmenium.—The hydrated acid does not take up any sulphur on digestion with sulphuret of ammonium. Ilmenium, mixed with sulphur in a flask and heated, does not combine with it; but when heated in an atmosphere of sulphur, it does. The sulphuret of ilmenium is best obtained by heating ilmenic acid to redness in the vapour of sulphuret of carbon; it burns in the atmosphere with a blue flame to sulphated ilmenic acid. 85·50 parts yielded 75·00 parts of ilmenic acid, which contain 59·79 ilmenium; the sulphur compound must consequently possess the following composition:—

Ilmenium	72·473	2 =	1573·18	77·32
Sulphur.....	27·527	3	602·12	27·68

On igniting ilmenic acid in the vapour of sulphuret of carbon, there is consequently formed, not IlS^2, but Il^2S^3; which is the more remarkable, as tantalic and titanic acids, according to the earlier experiments of Rose, are converted under similar circumstances into compounds corresponding to the acids.

Chloride of Ilmenium.—Ignited ilmenic acid does not dissolve in sulphuric acid; the hydrate leaves, on evaporation with concentrated sulphuric acid, a transparent horny mass, which on treatment with

water divides into aqueous sulphuric acid and insoluble sulphated ilmenic acid. It continually parts with acid on long-continued washing, becoming converted into hydrated ilmenic acid. Some sulphated ilmenic acid, which had been washed for a very long time, consisted, after being dried at 122°, of 75·63 ilmenic acid, 7·69 sulphuric acid, and 14·68 water.

Ignited ilmenic acid fuses with 6 times its weight of bisulphate of potash or soda to a clear mass, which deposits on the addition of water insoluble sulphated ilmenic acid, which retains very tenaciously some sulphate of potash. Ignited ilmenic acid, on fusion with the bisulphate of ammonia, is only imperfectly dissolved; the hydrate, on the contrary, entirely, forming with it on solidification a clear mass, from which sulphated ilmenic acid subsides in transparent lumps on solution. This sulphated ilmenic acid dissolves in warm muriatic acid; but if the sulphuric acid has been removed by long-continued washing with water, the hydrate no longer dissolves. To obtain ilmenium dissolved in muriatic acid, the chloride must be used; this latter is obtained on igniting ilmenic acid with charcoal in a current of dry chlorine, as a volatile sulphur-coloured mass, which quickly becomes white in the air; it attracts moisture, and is converted, with evolution of muriatic vapours, into hydrated ilmenic acid. When thrown into water, it is decomposed with a hissing noise, and the liquid retains perchloride of ilmenium in solution. When heated alone, the chloride of ilmenium undergoes decomposition; at first a dark yellow, more volatile and easily fusible perchloride, probably $IlCl^3$, passes over, then the undecomposed chloride, and the residue is an oxychloride. Heated in a current of dry hydrogen, the chloride of ilmenium passes over unaltered. Its composition has already been given above.

Chloride of Ilmenium and Ammonia is obtained by treating the chloride of ilmenium with dry ammonia; it is yellow, and is decomposed by heat into chloride of ammonium and ilmenium.

Ilmenates.—Hydrated ilmenic acid does not dissolve in ammonia or in carbonate of soda; it is only on fusing the acid with the latter that the carbonic acid is expelled. When hydrate of soda is fused with ilmenic acid and the mass boiled with water, a residue is left of ilmenate of soda, which is insoluble in water containing alkali, but dissolves in pure boiling water, from which it may then be readily obtained in crystals containing water; both the solution and the crystallized salt absorb carbonic acid from the atmosphere, the latter becoming thereby white and partially insoluble. When the crystals are heated to redness, they turn dark yellow, lose their water without decrepitation or changing their form, and remain pale yellow even after cooling. 100 parts of this salt lost 28·90 parts water; its composition is consequently—

$NaO\ IlO^2$.....	71·10	1 =	1379·32	71·04
HO	28·90	5	562·50	28·96

100 parts of ignited crystallized ilmenate of soda were fused with 6 times the amount of bisulphate of ammonia, the transparent mass heated with water, and the eliminated ilmenic acid collected, ignited

and weighed; it amounted to 71·607; the anhydrous salt consisted therefore of 71·607 acid and 28·393 soda; theory requires, taking $IlO^2 = 989{\cdot}590$, 71·75 per cent. of ilmenic acid. The crystallized ilmenate of soda is well adapted for preparing the other salts by double decomposition. Ilmenate of lithia is very sparingly soluble; ilmenate of baryta, strontia and lime are insoluble, colourless, transparent, flocculent precipitates. The combinations of ilmenic acid with yttria, protoxide of manganese, oxide of lead and silver, resemble that with baryta; the ilmenate of alumina is mucilaginous and transparent; the ilmenate of the peroxide of iron is of a light yellow, like milk of sulphur; the persalt of copper and the ilmenate of the oxide of chromium are apple-green. The ilmenate of soda is not precipitated by an excess of oxalic or tartaric acid; the hydrate is consequently soluble in these acids; acetic acid, on the contrary, produces a turbidness.

Yttroilmenite forms rectangular prisms terminated by a rhomboidal octahedron; the crystals are apparently isomorphous with columbite. Two analyses yielded the following results:—

	I.	Oxygen.		II.	Oxygen.	
Ilmenic acid	57·813	11·72	14·66	61·33	12·43	13·02
Titanic acid	5·901	2·34		1·50	0·59	
Protoxide of cerium Oxide of lanthanium	2·273	0·32		traces		
Yttria	18·302	3·24	6·95	19·74	3·49	6·67
Protoxide of uranium	1·869	0·20		5·64	0·62	
Protoxide of iron	13·613	2·99		8·06	1·77	
Protoxide of manganese	0·310	0·06		1·00	0·22	
Lime	0·500	0·14		2·08	0·57	
Water	...	...		1·66	...	
	100·581			101·01		

As the amount of oxygen in the acids is nearly twice that of the bases, yttroilmenite must be a neutral salt consisting of equal atoms of acid and base, according to the formula $RO \begin{cases} IlO^2 \\ TiO^2 \end{cases}$.

Journ. für Prakt. Chem., xl. p. 457.

On Camphoramminic Acid and Camphorimide, and some other Amidogen Acids. By M. Laurent.

Malaguti was the first chemist who examined the action of ammonia upon anhydrous camphoric acid; and he found that the salt which is produced by the action of the bicarbonate of ammonia or liquid ammonia upon anhydrous camphoric acid does not decompose the salts of copper, lead and silver; on slow evaporation the solution becomes syrupy, and finally yields a white crystalline mass. If it be decomposed by an acid, neither anhydrous camphoric acid nor the hydrate is obtained, but a viscous mass, which after some time solidifies. The combination of the anhydrous camphoric acid with ammonia has the formula $C^{20}\,H^7\,O^3, HO, NH^3$; the copper salt prepared from the anhydrous acid is $C^{20}\,H^7\,O^3, CuO$.

The statements of Malaguti have been confirmed by Laurent,

who moreover observes that the anhydrous camphoric acid does not combine with ammoniacal gas; but if the two bodies dissolved in absolute alcohol be allowed to act upon one another at a boiling temperature, a crystalline ammonia salt separates after some time. The decanted mother-ley yields more on evaporation. It was washed with a little cold absolute alcohol, and dried; it gave—

	Found.		Calculated.
Carbon	51·1	20 =	51·2
Hydrogen	9·3	22	9·4
Nitrogen	11·7	2	11·9
Oxygen	27·9	8	27·5

This salt is, according to Laurent, camphoramminate of ammonia, and is consequently isomeric with camphorate of ammonia, but it contains 1 equiv. of water of crystallization.

Laurent states that the absorbed ammonia is contained in the compound in two different conditions; one-half of it is precipitated by chloride of platinum, while the other continues in the compound, and forms part of a new acid, which enters into combination with metallic oxides. Laurent obtained, by the addition of chloride of platinum to an alcoholic solution of 1 grm. of the above compound, ammonio-chloride of platinum which contained 0·400 grm. platinum, corresponding to 5·7 per cent. nitrogen, while if the whole of the ammonia had been precipitated he must have obtained 11·9 per cent. The solution filtered from the ammonio-chloride of platinum left on evaporation, which was undoubtedly continued too far, a vitreous mass, and not camphoramminic acid, as the author had expected.

Camphoramminic Acid.—When a concentrated solution of camphoramminate of ammonia is mixed with muriatic acid, a syrupy precipitation results, as stated by Malaguti. In the course of twenty-four hours a small crystalline deposit of camphoramminic acid separates from the decanted solution; but if a dilute solution of the ammonia salt be used, no syrup is formed; and the solution, evaporated at a gentle heat, yields crystals of camphoramminic acid, which are recrystallized from weak alcohol. It is colourless, pretty soluble in hot water, less so in cold; it is still more soluble in alcohol, from which it crystallizes in large rectangular prisms, which are quite perfect and transparent. If some of it be melted upon a watch-glass, a part solidifies on cooling in rhombic crystals, while the remainder remains for a long time liquid, and yields a transparent vitreous mass, which is no longer camphoramminic acid. With ammonia it again produces camphoramminate of ammonia. Its composition is—

Carbon	60·0	20 =	60·3
Hydrogen	8·4	17	8·5
Nitrogen	7·4	1	7·0
Oxygen	24·2	6	24·2

This formula represents consequently 2 equivs. anhydrous camphoric acid + 1 equiv. ammonia. The preceding ammonia salt is accordingly $C^{20} H^{17} NO^6, NH^3 + 2\,aq.$

Camphoramminate of Lead.—When a cold aqueous solution of the ammonia salt is poured into acetate of lead, no precipitate is formed; nor is this the case when boiling concentrated solutions of the two salts are mixed in alcohol; on cooling, however, small needles of this salt separate, which are quickly rinsed with alcohol and dried; it is too easily soluble to admit of being washed perfectly. On analysis it yielded 33·0 per cent. lead. The formula $C^{20}H^{15}NO^5 + PbO$ requires 34·5 per cent. lead.

Camphoramminate of Silver.—No precipitate is obtained on mixing boiling alcoholic solutions of camphoramminate of ammonia and nitrate of silver. On cooling, the liquid congeals to a transparent jelly, which appears under the microscope to consist of a tissue of very long needles, which are so thin that they can scarcely be perceived with a magnifying power of 300. The analysis gave 34·7 per cent. silver; the formula $C^{20}H^{16}NO^5 + AgO$ requires 35·1 per cent.

Camphorimide.—This substance may be obtained by heating camphoramminate of ammonia to 302°–320°, by distillation of this salt, or lastly, by distillation of camphoramminic acid. In the first case water and ammonia are disengaged, leaving a colourless substance, which solidifies on cooling without crystallizing. It is dissolved in boiling alcohol, from which it crystallizes on cooling. Camphorimide is colourless, volatile at a very high temperature, and can be distilled without decomposition. On evaporating a weak alcoholic solution, it is gradually deposited as a transparent gummy mass, which solidifies in the course of twenty-four hours into opake warty masses. When heated with potash, it gives off ammonia. It dissolves at a gentle heat in concentrated sulphuric acid; and upon the addition of a few drops of water, it forms a white crystalline deposit. On analysis it yielded—

Carbon	65·9	20	= 66·3
Hydrogen	8·1	15	8·3
Nitrogen.....	..	1	7·7
Oxygen	..	4	17·7

Camphoramminate of ammonia lost 21·6 per cent. of water and ammonia at 302°; if the reaction were as follows,

$$C^{20}H^{22}N^2O^8 - H^4O^4 - NH^3 = C^{20}H^{15}NO^4,$$

the loss should amount to 22·6.

Salts of Anhydrous Camphoric Acid.—Malaguti examined the copper and potash salts; both possess the same composition as the ordinary camphorates, but different properties. Laurent boiled milk of lime with anhydrous camphoric acid, and obtained on evaporation white laminæ of a salt which contained 20·1 per cent. of lime or 14·3 per cent. calcium; this salt, which had subsided from a very concentrated solution, appeared, after having been dissolved in boiling water, to become insoluble. After long boiling, however, it was filtered and again evaporated, when the liquid, after it had become very concentrated, deposited nothing; the salt had therefore again become very soluble. Upon the addition of alcohol, a white preci-

pitate was formed, which consisted of microscopic needles, and contained 19·7 per cent. lime or 14 per cent. calcium. The formula $C^{40}H^{27}O^{14}Ca^3$, which requires 13·6 per cent. calcium, agrees best with this result. These experiments however are evidently not sufficient to establish the formula of this body.

According to this, anhydrous camphoric acid appears to act the part of a hydrated acid like isatine.

Lactamminic Acid.—When anhydrous lactic acid, $C^6N^5O^5$, dissolved in absolute alcohol, is treated with ammoniacal gas, a compound, $C^6H^5O^5 + NH^3$, is obtained, according to Pelouze, in which the ammonia can be detected by the usual reagents. The author did not succeed in obtaining this crystalline substance. After removing the excess of ammonia by boiling, he added chloride of platinum to it, when ammonio-chloride of platinum was immediately formed; this was separated by filtration, and the solution boiled for an hour, when a fresh precipitate of ammonio-chloride of platinum was formed. Hence the anhydrous lactate of ammonia contained the ammonia in two different states, and is analogous to the camphoramminate of ammonia. The formula for anhydrous lactic acid should accordingly be doubled*.

The author endeavoured to obtain the lactamminate of ammonia by evaporation of the solution, which left a substance crystallizing in laminæ, extremely soluble in water and alcohol, and which proved on analysis to be lactamide.

The lactamminate of ammonia yields therefore already on evaporation lactamide, analogous to the isamminate of ammonia, while the camphoramminate of ammonia gives camphorimide only on fusion.

Tartraminic Acid.—This acid has been still less perfectly examined than the preceding one. When a current of ammoniacal gas is passed over anhydrous tartaric acid moistened with alcohol, two strata are obtained, the upper one of which is alcohol, while the inferior one contains tartraminate of ammonia. This salt is insoluble in alcohol, but dissolves in water in every proportion. When heated it parts with water, and acquires a faintly crystalline structure. Its aqueous solution does not decompose chloride of calcium; but on the subsequent addition of alcohol an abundant precipitate is formed, which becomes solid when warmed. The tartraminate of lime yields no precipitate with chloride of platinum, leaves on burning 30 per cent. carbonate of lime, and contains 1·9 per cent. nitrogen; these numbers, however, are by no means in accordance with theory. On boiling it is gradually decomposed into bitartrate of lime and ammonia, which latter may then be detected by chloride of platinum. —*Ann. der Chem. und Pharm.*, lx. p. 326.

On Mucic Acid and the Mucates. *By* R. Hagen.

The following experiments lead the author to the conclusion, that the formula $C^6H^4O^7 + HO$, advanced by Malaguti for mucic acid,

* The recent researches of Maddrell and Engelhard likewise show that lactic acid must be regarded as a bibasic acid.—Ed.

must be doubled, as suspected by Liebig, and the acid considered as bibasic. The potash, soda, baryta and lime salts would contain half atoms of water of crystallization if Malaguti's formula were retained. With respect to the preparation of this acid, it results from the experiments of the author that oxalic acid is always formed as a collateral product by the action of nitric acid upon milk-sugar, and indeed at the direct expense of the milk-sugar; less from the mucic acid. The maximum of mucic acid is obtained by employing a moderately-strong nitric acid; concentrated acid, on the contrary, probably converts a portion of it into oxalic acid. A very dilute nitric acid converts milk-sugar almost exclusively into oxalic acid. The generally received opinion, therefore, that milk-sugar, $C^{12}H^{12}O^{12}$, passes into mucic acid on treatment with nitric acid by the fixation of 6 atoms of oxygen and elimination of 2 atoms of water, is not satisfactory.

15 grms. of milk-sugar were boiled with dilute nitric acid (1 part acid of 1·35 spec. grav. and 4 parts water), replacing the evaporated acid. After ten hours' boiling, during which time apparently but few red vapours had formed, the experiment was discontinued. In the course of several days but a small quantity of mucic acid separated from the liquid, which on the other hand contained a large amount of oxalic acid. 29·22 grms. milk-sugar were digested with 8 oz. of nitric acid of 1·35 spec. grav. and 2 oz. of water until the evolution of gas began to cease. After cooling, water was added to the liquid, in order to separate the mucic acid, the quantity of which amounted to 9·03 grms. Subsequently 1·463 more mucic acid separated from the mother-ley; the liquid filtered from this was saturated with carbonate of ammonia, then acetic acid added to it and heated to boiling, upon which the oxalic acid was precipitated with chloride of calcium, while the mucate of lime was held in solution by the acetic acid. The quantity of oxalic acid obtained, calculated as anhydrous acid, was 1·78 grm.; consequently 100 parts of milk-sugar had furnished 35·89 mucic acid and 4·35 per cent. of anhydrous oxalic acid. In another experiment, which was made in the same manner and with exactly the same quantities, 35·4 per cent. mucic acid and 7·13 per cent. oxalic acid were obtained. In one experiment with concentrated nitric acid, 15 grms. of milk-sugar were boiled for several hours with ten times the weight of acid, and after cooling treated as above; there was obtained 4·31 mucic acid and 3·82 grms. anhydrous oxalic acid; consequently 100 parts of milk-sugar yielded 28·73 per cent. mucic acid and 14·25 per cent. anhydrous oxalic acid.

Pure mucic acid is but little acted upon by concentrated nitric acid, for on boiling a small quantity for six hours with concentrated acid, nearly the whole was obtained unaltered from the liquid, which contained but a small amount of oxalic acid. The above experiments show that, under the most favourable circumstances, from 100 parts of milk-sugar containing 40 per cent. carbon, only 35·9 parts mucic acid containing 12·46 carbon, could be obtained; and that consequently scarcely the third part of the milk-sugar is con-

verted into mucic acid; the remainder is changed partly into carbonic acid and partly into oxalic acid.

Neutral mucate of potash, air-dried and dried at 212° = 2KO + $C^{12} H^8 O^{14}$ + HO; dried at 302° = 2KO + $C^{12} H^8 O^{14}$ is obtained on saturating mucic acid with potash or the carbonate. It is deposited from the boiling-hot solution in white crystalline granules. At 302° it becomes anhydrous, assuming a straw colour; but when dissolved in a little hot water, the hydrated salt is again deposited on cooling. In the following analysis, I. is of salt dried in the air, II. and III. dried at 212°, IV. dried at 302°:—

	I.	II.	III.			
Mucic acid ..	..	..	..	1	=2417·06	
Potash	31·952	31·790	32·001	2	1179·84	31·82
Water	..	..	..	1	112·48	

	IV.			
Mucic acid	..	1	2417·06	
Potash	32·256	2	=1179·84	32·256

The mother-ley of the mucate of potash, even when very pure mucic acid is used, is brown, and, when mixed with nitrate of silver and some ammonia, reduces the silver in the form of a metallic mirror. On treating a portion of this brown mother-ley with acetic acid and concentrating, in order to ascertain whether the reaction was owing to an admixture of saccharic acid, no bisaccharate of potash separated.

Bimucate of potash, dried at 212° and in the air, = KO HO + $C^{12} H^8 O^{14}$ + 2HO. Carbonate of potash is saturated with mucic acid, and a further quantity of acid equal to that consumed added to the solution; it forms minute transparent crystals, which dissolve more readily in water than the neutral salt, and consist of—

Mucic acid ..	..	..	..	1	=2417·06	
Potash	17·598	17·343	17·391	1	589·92	17·64
Water	..	..	..	3	337·44	

Mucate of soda, 2NaO + $C^{12} H^8 O^{14}$ + 9HO, dried at 212°, = NaO + $C^{12} H^8 O^{14}$ + HO. The salt with 9 atoms of water separates from a solution of mucic acid saturated with carbonate of soda on slow evaporation in large transparent crystals, which effloresce in the air. If the solution of this salt be evaporated quickly, a white powder separates, which has the same composition as the salt dried at 212°, and on re-solution and slow evaporation is converted into the salt with 9 atoms of water. In general a mixture of the two salts is obtained in preparing the mucate of soda, but they are easily separated by suspension:—

Mucic acid....	..	1	= 2417·06	
Soda	18·726	2	781·80	18·57
Water.....	..	9	1012·30	

The crystals dried at 212° gave 23·58–23·75 per cent. soda. The above formula with 1 equiv. water requires 23·661 per cent.

Mucate of magnesia, dried at 212°, = 2MgO + $C^{12} H^8 O^{14}$ + 4HO.

A solution of mucic acid is not precipitated by sulphate of magnesia; but a solution of the mucate of ammonia produces a precipitate, the quantity of which is increased by boiling. The salt contained 15·435–15·125–15·45 magnesia.

Mucate of lime, dried at 212°, $= 2CaO + C^{12} H^8 O^{14} + 3HO$. A solution of chloride of calcium is not precipitated by the free acid, but mucate of ammonia throws down neutral mucate of lime, which still contains 3 equivs. water after desiccation at 212°. The salt dissolves in acetic acid. It yielded 20·47–20·50 lime; the above formula requires 20·54.

Mucate of baryta, $2BaO + C^{12} H^8 O^{14} + 3HO$. A solution of chloride of barium is not precipitated by the free acid, but mucate of ammonia throws down a precipitate, which is crystalline when the solutions are agitated with a glass rod. A considerable quantity more is deposited on boiling the liquid. This salt likewise contains 3 equivs. water after desiccation at 212°. It yielded 41·36–41·38–40·86 per cent. baryta; the formula requires 41·00.

Mucate of copper, dried at 212°, $= 2CuO + C^{12} H^8 O^{14} + HO$. It is precipitated as a bluish-white powder from sulphate of copper by mucate of ammonia; it is insoluble in water, and contained 27·959 per cent. oxide of copper; the formula requires 28·15.

Mucate of the protoxide of iron, dried at 212°, $= FeO + C^{12} H^8 O^{14} + 4HO$. From a solution of the protosulphate of iron, mucate of soda or ammonia throws down a yellowish-white powder, which does not change by exposure to the air, and still contains 4 atoms of water after desiccation at 212°. When heated to 302°–320°, it is converted into a brown mass, which ignites spontaneously on exposure to the air. It yielded 23·384–23·613 per cent. protoxide of iron.

Mucate of lead, dried at 212°, $= 2PbO + C^{12} H^8 O^{14} + 2HO$; dried at 302°, $= 2PbO + C^{12} H^8 O^{14}$. This salt is obtained by precipitating a solution of mucic acid with acetate of lead. The statement that the mucate of lead loses a portion of its acid on treatment with ammonia was not confirmed by the author. In the salt dried at 212°, 51·582–51·12–51·83 per cent. oxide of lead were found; the above formula requires 51·35. The salt dried at 302° yielded 54·097 per cent.; theory requires 53·59. When mucate of ammonia is precipitated with acetate of lead, a mucilaginous precipitate is obtained, which is slightly soluble in water, and always contains acetic acid and a varying amount of lead.

Mucate of silver, dried at 212°, $= 2AgO + C^{12} H^8 O^{14}$, possessed exactly the composition assigned to it by Malaguti, and contained 54·79 per cent. silver.—Poggendorff's *Annalen*, lxxi. p. 531.

On the Atomic Weight of Tantalium, Niobium and Ilmenium. *By* R. Hermann.

Berzelius determined, in his investigation, the equivalent of tantalium to be 1148·365. Owing to the alterations which the equivalents of sulphur and chlorine have recently undergone, he has corrected this number and made it 998·365. Berzelius regards tantalic

acid as Ta^2O^3; if we suppose the acid to consist of 1 atom of tantalium to 2 of oxygen, we obtain, according to the recent equivalents, Ta = 1331·15, while with the older equivalents we have 1531·15. Now the composition of the chloride of tantalium analysed by the author agrees with the new equivalent, for chloride of tantalium, prepared from Finland tantalite, gave 40·00 chlorine to 69·36 ignited tantalic acid; we accordingly obtain, on calculating the atom from the amount of chlorine, the number 1329·84, and from the tantalic acid 1337·19; on an average, therefore, 1333·565. The amount, calculated from the crystallized tantalate of soda, does not agree so well, for this salt contained in the anhydrous state:—

TaO^2	80·115	80·28	Mean....	80·198
NaO	19·885	19·72	Mean....	19·802

The equivalent of tantalium, calculated from this, is 1378·45; and the excess to which this difference is due probably results from the retention of a small amount of sulphuric acid and alkali, of which it is extremely difficult to purify the acid. The chloride of tantalium, prepared in the same manner as the chloride of ilmenium and crystallized in yellow prisms, gave—

Ta	60·00	1	=	1331·15	60·02
Cl.....	40·00	2		886·56	39·98
$TaCl^2$				2217·71	

Tantalate of soda, prepared in the same way as the crystallized ilmenate of soda, contains 5 equivs. water.

Niobic Acid was prepared from aeschynite; it yielded, on fusion with bisulphate of soda, a perfectly clear solution with a little water, and was therefore free from tantalic and ilmenic acids. From the properties of pelopic acid being as yet but imperfectly known, the author is not certain as to the absence of this acid; nevertheless the following equivalent will serve to distinguish the compounds of niobium from those of ilmenium. The chloride of niobium, prepared in the same way as the chloride of ilmenium, crystallizes in pinnately-grouped prisms. It gave, on decomposition with water and bicarbonate of soda—

Nb	58·33	1	=	1251·53	58·54
Cl.....	41·67	2		886·56	41·46
NbCl				2138·09	

Crystallized niobate of soda gave in the anhydrous state—

NbO^2	78·96	1	=	1451·53	78·84
NaO.....	21·04	1		389·73	21·16

The salt contains 29·68 per cent. water, which corresponds to the formula $NaO\ NbO^2 + 7HO$.—*Journ. für Prakt. Chem.*, xl. p. 877.

On the Composition of Vitelline. *By* Henry M. Noad, Esq.*

Vitelline has been analysed by Jones, by Dumas and Cahours, and by Baumhauer, but their analyses do not agree with each other:—

* Communicated by the Author.

	* Jones, C = (76·437).		Dumas and Cahours, (C = 75).		Baumhauer, dried at 248°.	
Carbon ..	53·72	53·45	51·89	51·31	53·23	53·56
Hydrogen	7·55	7·66	7·07	7·37	7·03	7·12
Nitrogen ..	13·60	13·34	15·02	15·03	15·97	16·09
Oxygen ..	23·13	25·55	26·02	26·29	23·25	22·75
Sulphur ..	..	..	..	..	0·52	0·48

The vitelline analysed by Jones and by Dumas and Cahours was prepared by digesting the yolks of hard-boiled eggs in alcohol and æther; the subject of Baumhauer's experiments was obtained by dissolving this substance in acetic acid and precipitating the clear filtered liquid by carbonate of ammonia.

M. Gobley, in his memoir 'On the Composition of the Yolk of the Egg†,' alludes to an analysis of vitelline which he prepared by exhausting the dried yolk with boiling alcohol; he does not give the numbers which he obtained, but merely states that his results agreed with those of Dumas and Cahours.

The disagreement between the results obtained by these chemists, particularly in the amount of nitrogen, induced me to undertake some new analyses, which I proposed should include also a determination of the sulphur. The substance was prepared by digesting the yolks of hard-boiled eggs carefully separated from the whites twice in strong boiling alcohol, and afterwards repeatedly in æther, until the latter passed through the filter colourless and the vitelline became quite white. It was dried for several hours in the water-bath at 212° until it ceased to lose weight; a portion was also dried at from 270° to 300°, at which temperature however it became coloured, a partial decomposition having probably taken place; the portion dried at 212° was of a very pale straw colour. I attempted also to prepare a specimen by Baumhauer's method, which according to Mulder is the only way of procuring vitelline free from cellular matter; but after repeated and protracted digestions with acetic acid, both strong and dilute, I obtained, on adding carbonate of ammonia to the filtrate, so very minute a precipitate that I despaired of obtaining a sufficient quantity for a thorough examination; nor did it indeed seem worth while to attempt it, as, according to Mulder's own statement, vitelline, when precipitated in this manner, contains ammonia, which would of course increase the proportion of nitrogen, the element, the per-centage amount of which I was most anxious to ascertain. It may be mentioned that Baumhauer analysed vitelline as prepared by Jones and by Dumas and Cahours. He found—

Carbon	52·99	52·95
Hydrogen	6·93	6·92

It is rather singular that he omitted to make a determination of the nitrogen.

* Mulder's Chem. of Vegetable and Animal Physiology, p. 303.

† Comptes Rendus, Sept. 29 and Nov. 3, 1845; and Chem. Gaz., vol. iii. pp. 443, 486.

According to M. Gobley, the yolk of egg yields on an average 16·557 per cent. of vitelline. Mulder assigns to it the formula $C^{40}H^{31}N^{5}O^{14}$, and he considers it to be a sulphuret of bioxide of proteine*. My experiments gave the following results:—

I. 0·4350 grm., by combustion with chromate of lead, yielded 0·860 grm. carbonic acid and 0·306 grm. water.

II. 0·4575 grm. gave 0·9035 grm. carbonic acid and 0·3175 grm. water.

III. 0·3950 grm., from a fresh preparation, gave 0·7835 grm. carbonic acid and 0·2785 grm. water.

IV. 0·5245 grm., burned with soda-lime according to the method of Will and Varrentrapp for the determination of nitrogen, gave 1·0880 grm. of double chloride of platinum and ammonium.

V. 0·4895 grm. gave 0·9805 grm. of double chloride of platinum and ammonium.

VI. 2·127 grms., mixed with nitrate of baryta and digested with fuming nitric acid according to the method of Weidenbusch for the determination of sulphur, gave 0·287 grm. sulphate of baryta.

VII. 2·801 grms., from another preparation, gave 0·354 grm. of sulphate of baryta.

These numbers correspond with the following per-centages:—

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon....	53·95	53·85	54·08				
Hydrogen..	7·84	7·71	7·83				
Nitrogen ..	..	..	..	13·02	12·6		
Sulphur ..	..	..	..	..	..	1·85	1·50

The carbon and hydrogen agree, it will be seen, very closely with the analyses of Jones; the nitrogen is somewhat lower; to control my own numbers, I have therefore compared them with those obtained by the new method of Peligot†; and as the figures thus obtained agree exactly amongst themselves and very closely with the previous determinations, it may perhaps be worth while to detail them, and to describe briefly the particulars of the manipulation.

The standard sulphuric acid employed was of the specific gravity 1·0504; the quantity of dry acid which a small bottle of about one cubic inch capacity contained was very accurately determined by precipitation with chloride of barium to be 15·8 grs., which agrees exactly with the theoretical amount calculated from the specific gravity by Dr. Ure's table. By a simple calculation it was ascertained that this quantity of dry acid is equivalent to 6·704 grs. of ammonia, or 5·521 grs. of nitrogen. The solution of lime in sugar was of such a strength that it required 54·25 divisions of the burette to neutralize exactly the bottle-full of the standard acid. The condensing apparatus employed is larger than it is usually made; it has three bulbs instead of two, and will hold about two-thirds of the contents of the bottle without being sufficiently full to excite any apprehension of the rushing back of the acid into the combustion-tube at the close of the operation.

* Chem. of Vegetable and Animal Physiology, pp. 303–316.

† Chem. Gaz., May 1, 1847.

I. 0·4880 grm. = 7·53 grs. of vitelline was burned with soda-lime, and the ammonia condensed in the standard acid, which after the combustion was finished was transferred to a beaker, and the apparatus rinsed out repeatedly with distilled water; the remainder of the acid in the bottle was then added, and the whole diluted to about half a pint, and a few drops of litmus added. 45 measures of the sugar-lime were required to saturate the acid. 9·25 measures (54·25–45) therefore represent the quantity of sugar-lime required to neutralize the sulphuric acid, equivalent to the ammonia given off by the substance; a simple calculation shows this to be equal to 0·941 gr. of nitrogen, or 12·5 per cent.

II. 0·6590 grm. = 10·17 grs. was burned; after the combustion 42 measures of the sugar-lime were required to saturate the acid; 54·25–42 = 12·25, which represents the sulphuric acid condensed by the ammonia; this gives 1·246 gr. for the amount of nitrogen, or 12·35 per cent.

In the next experiment a different standard acid was employed and a fresh preparation of vitelline analysed. The acid was equivalent to 4·004 grs. of ammonia, or 3·297 grs. of nitrogen; and it required for neutralization 32 divisions of sugar-lime, which was also a fresh preparation.

III. 0·469 grm. = 7·24 grs. was burned; after the combustion 23·25 measures of sugar-lime were required to saturate the acid; 32–23·25 = 8·75, which represents the sulphuric acid neutralized by the ammonia; this gives 0·9016 for the ammonia in the substance, or 12·45 per cent.

These results are a trifle below the truth, which must necessarily be the case from the very principles of the method, it being always necessary to add a slight excess of the alkaline solution in order to see, by the change of the liquid from red to blue, when neutralization has taken place. It is true that when we are experimenting with a perfectly colourless acid, the smallest addition of the lime solution above that required for the perfect neutralization of the acid immediately determines the blue colour; but after the acid has served to condense the ammonia given off by the combustion of an organic substance with soda-lime, it is always more or less coloured; nor can a considerable tinge of yellow be prevented, although it is much diminished by using a long combustion-tube and a great excess of soda-lime; this colour renders it difficult to hit the precise moment when neutralization takes place; if the sugar-lime be added until the liquor becomes distinctly blue, a deficiency of nitrogen, amounting nearly to *one* per cent., may easily occur, as I have ascertained by numerous experiments, and it is only practice that will enable the operator to stop exactly at the proper time. The best practical rule that can be given, is to use a long combustion-tube, to keep its anterior portion very hot, and to dilute the acid considerably with water previous to adding the alkaline solution. The above results, as compared with those obtained on Will and Varrentrapp's plan, will show the degree of reliance to be placed in the new method, which possesses two great advantages—œconomy of time, the

whole operation not taking more than three-quarters of an hour; and œconomy of money, the expense of alcohol and æther being avoided. I may observe, lastly, that the alkaline solution recommended by Peligot is much better than carbonate of potash or soda, inasmuch as we avoid the presence of carbonic acid, the evolution of which would interfere with the immediate change of colour.

With respect to Weidenbusch's method of determining sulphur*, it is easy to be deceived as to the time required for the complete oxidation of this element even under the favourable circumstances in which the experiment is made; nor does there seem any means of ascertaining when the destruction of the organic substance is complete. I made several experiments on this point, and I found that even after a digestion of several hours, and the successive additions of fuming nitric acid, the mass took fire on drying, involving the danger of a projection of a portion by deflagration. In the experiments above-quoted, the mixture of vitelline and nitrate of baryta was digested with fuming nitric acid for six hours, the evaporated acid being from time to time replaced; it nevertheless took fire on drying; and although there was no loss by deflagration, the quantity of sulphate of baryta obtained may, according to Weidenbusch, have been smaller than it should have been, the whole of the sulphur not having been converted into sulphuric acid. However this may be, the amount of that element yielded by the two experiments, which do not differ very widely from each other, is more than *three times* greater than was found by Baumhauer, though they agree very closely with that found by Verdeil and Rüling† in their analyses of albumen from eggs.

1 New Milman Street, Russell Square, Oct. 9, 1847.

On a Substance occurring in the Perisperms of Seeds.
By M. von Baumhauer.

According to the recent experiments of Mulder and Harting, vegetable ivory (the seed of *Phytelephas macrocarpa*), which had been previously examined by Connell, Schultz and the author, consists of two substances, one of which is cellulose. To isolate the other body, the powder of the vegetable ivory was exhausted with cold and boiling water, and then dried and triturated in a glass mortar with a mixture of 2 parts sulphuric acid of 1·85 spec. grav. and 1 part water, which is some time before it colours the powder; the jelly is then poured on a funnel stopped with finely-powdered glass. The clear filtered solution afforded with water a flocculent snowy-white precipitate, which was first freed from sulphuric acid by cold water, then exhausted with boiling water, ammonia, alcohol and æther, and dried at 284°. A further portion of the white flocculent substance was separated by alcohol from the diluted sulphuric solution. It yielded on analysis—

* Liebig's Annalen for March; and Chem. Gaz., June 1, 1847.
† Chem. Gaz., vol. iv. p. 363.

Carbon	43·99	44·06	43·84	43·89
Hydrogen	6·32	6·28	6·29	6·15

To ascertain whether the substance in question occurred in the horny albuminous coating of coffee-berries, the pounded berries were first digested for a considerable length of time with water, acetic acid, alcohol and æther, dried, and treated as above described with sulphuric acid. The snowy-white precipitate afforded after purification—

Carbon	43·89	43·85	43·87	43·77	48=43·84
Hydrogen	6·24	6·27	6·25	6·21	41 6·23
Oxygen	..	..	..	..	41 49·93

This encrusting substance is soluble in sulphuric acid, from which it is precipitated by water and alcohol, but not by ammonia. Sulphuric acid of 1·85 spec. grav. first becomes purple and then brown when mixed with it. Nitric acid converts it into oxalic acid; concentrated muriatic acid dissolves it slowly, and is at length coloured brown by it. It is not soluble in ammonia; it swells in strong caustic potash, and dissolves entirely on the addition of water. It is precipitated, but not entirely, by acetic acid from a concentrated solution of caustic potash. On burning, it smells like cellulose, and yields an easily-combustible cinder.—Buch. *Rep.*, xlv. p. 220.

Observations on Prof. Mulder's *Researches on the Bile.* *By* Geo. Kemp, M.D. Cantab.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Sir,—I have anxiously waited for the conclusion of your abstract of Professor Mulder's researches on the bile, in order to lay before you certain reasons which may lead to a considerable modification of the Professor's theoretical views. It will not however be seemly for me to enter into a lengthy examination of the subject before I have made myself acquainted with the details as given in the original; indeed I should not trouble you with the following preliminary statement were it not for the conviction that upon a correct view of the composition of the bile depends the development of the occult processes of digestion, particularly that stage in which the *formation of fat* and the conversion of the food in general into *chyle* take place. The illustrious Professor will, I am sure, admit this as an apology for my thus publicly differing from him.

At page 321 of the present volume of your Journal, a body is described as containing 18·21 per cent. of baryta, the organic portion of this body being as follows:—

Carbon	72·79
Hydrogen	9·97
Oxygen	17·24
	100·00

Proceeding in the usual manner with these data, which we must receive as results obtained by one of the most experienced of living

analysts, we obtain a formula widely differing from that proposed, $C^{50}H^{36}O^6 + 3\frac{1}{2}HO$. Such a body, whether consisting of one organic group or several, would require in combination 14·4 per cent., or if we consider it anhydrous, 15·3 per cent. of oxide of barium. In the opinion of Prof. Mulder, this body is a mere mechanical mixture, and therefore of little relative importance; it may however be suggested that, in evaporating the resinous body to dryness with caustic barytes, a metamorphosis, analogous to what would occur with caustic potash, is hazarded, and could hardly be avoided; at page 323 of the same number we find however a body denominated fellinic acid, which is considered sufficiently eliminated to determine its atomic weight with tolerable accuracy; the data are as follows; baryta, 8·19 per cent.:—

Carbon	70·73
Hydrogen	9·78
Oxygen	19·49
	100·00

The combining weight, as deduced from the oxide of barium, is 10573 for the barytic salt, or 9706 for the isolated electro-negative body, which leads to the formula $C^{46}H^{38}O^9$, and gives on calculation—

Carbon	70·76
Hydrogen	9·74
Oxygen	19·50
	100·00

I think, Sir, you will agree with me that a closer accordance of theory and fact rarely occurs; the formula proposed by Prof. Mulder, $2(C^{50}H^{40}O^{10}) + HO + BaO$, requires 7·5 of baryta. Although compelled thus far to differ from the Professor, I perfectly accord to his opinion that the bile (ox-bile at least) may be expressed by the elements of taurine, ammonia and the "*tertium quid*" just alluded to; but must solicit a little space in some future number of your Journal for the explication of my views, with some new analytical facts on this interesting subject.

I have the honour to remain, Sir,

Your very obedient Servant,

Ellenbrook, Isle of Man,
Oct. 8, 1847.

Geo. Kemp, M.D. Cantab.

On some new Compounds obtained by the Action of Chlorine upon Pyroxylic Spirit. By J. Bouis.

The author is led from his experiments to suppose that the chlorocyanic æther and the chlorocyanate of methylene described by Aimé have never been obtained, and that this subject requires further investigation. He then observes, that chlorine, by acting upon pyroxylic spirit, may give rise to methylal $C^6H^8O^4$, or an analogous body, which is again decomposed under the influence of the chlorine into hydrochloric acid, carbonic acid, and a volatile cry-

stalline body insoluble in water, and which he calls chloromesitate of methylene. The reaction is indicated by the equation—

$$2(C^6 H^8 O^4) + Cl^8 = C^{10} \begin{matrix} H^{10} \\ Cl^2 \end{matrix} O^4 + 2CO^2 + H^6 Cl^6.$$

On examining subsequently the action of chlorine upon the crystalline product dissolved in pyroxylic spirit, an oily liquid was obtained which possessed the composition of terchlorated acetone $C^6 \begin{matrix} H^3 \\ Cl^3 \end{matrix} O^2$, and then a crystalline body soluble in water, represented by the hydrated quadrichlorated acetone $C^6 \begin{matrix} H^2 \\ Cl^4 \end{matrix} O^2$, 8HO. This last body parts with 8HO, and gives rise to an excessively volatile liquid with the composition $C^6 \begin{matrix} H^2 \\ Cl^4 \end{matrix} O^2$.—*Comptes Rendus*, Aug. 9, 1847.

PATENT.

Patent granted to Alexander McDougall, *for Improvements in the Manufacture of Glue.*

The first part of this invention consists in drying glue, by the employment of currents of air artificially dried, either by heat or by means of any of the ordinary drying compounds, such as concentrated sulphuric acid or fused chloride of calcium. The drying chamber, containing the glue, is furnished at one end with a flue, or other means of creating a draft; and the dried air being introduced at the other end, is thus caused to traverse the surface of the glue.

The second part of this invention consists in procuring useful products from the refuse of the glue manufacture, termed "scutch," which is composed of lime, fatty acids, hair, and other animal and earthy substances. The scutch is introduced into a vessel containing water, and is agitated therein until the water assumes a milky appearance, and then the water is drawn off. This washing is repeated till the water remains colourless; and then the hair, bone and sand remaining in the vessel are removed, preparatory to the introduction of a fresh portion of scutch. The different liquors resulting from washing the scutch are allowed to stand until the substances suspended therein have subsided; after which the water is drawn off and the deposit treated with an acid. The acid preferred is dilute muriatic acid, which is to be added so long as there is any indication of alkaline reaction; but other acids, capable of separating the lime from the fatty matters with which it is combined, may be used. The salt of lime and the fatty matters are then separated in the ordinary manner. The useful products obtained by this process are hair, fatty matters and salts of lime; the latter may be used as manure, and for other purposes.—Sealed Jan. 14, 1847.

THE CHEMICAL GAZETTE.

No. CXXI.—November 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Cobalticyanic Acid and its Salts. *By* C. ZWENGER.

THE best method of preparing this acid is by decomposing the cobalticyanide of copper with sulphuretted hydrogen, which is very easily effected; sulphuret of copper separates, and on evaporating the liquid an acid analogous to the ferridcyanic acid is obtained, which the author calls cobalticyanic acid. The acid may also be obtained by separating it immediately from the cobalticyanide of potassium by means of sulphuric or nitric acid. The solution of cobalticyanide of potassium with excess of nitric acid is evaporated to dryness, and the residue exhausted with absolute alcohol, in which the cobalticyanic acid dissolves. It may be procured in a similar manner from the salt decomposed with sulphuric acid. From an aqueous solution the acid crystallizes in small, shining, transparent, colourless needles; it has a strong acid taste and reaction, neutralizes bases very completely, and combines with several metals even at the ordinary temperature, for instance with finely-divided zinc or iron, with disengagement of hydrogen. It absorbs moisture from the atmosphere and deliquesces. Its solution may be boiled without experiencing any material decomposition; it gives off but a very faint odour of prussic acid even on boiling; and when it has been evaporated perfectly to dryness, it leaves on re-solution but a mere trace of residue. It dissolves, as previously observed, in alcohol, but is insoluble in anhydrous æther. At 212° the crystallized acid parts with water without undergoing further change; at a somewhat higher temperature prussic acid is given off, the acid becomes yellow, and no longer dissolves wholly in water. At 374° it becomes green, which with a gradually increasing temperature slowly passes into blue, and at 482° the residue is perfectly blue. This blue residue very quickly loses its colour when placed in contact with moist air or water, and becomes reddish or brown according as the decomposition took place with access of air or the contrary. On heating the acid still more strongly, the blue colour disappears with disengagement of carbonate and prussiate of ammonia, the mass takes fire, sends off a shower of sparks, and there is left a black residue of carburet of cobalt. This carburet resists the action of the strongest acids most tenaciously, and can only be oxidized by being

ignited in a current of oxygen. In all the compounds described in this treatise, the cobalt, both when it had to be determined alone or at the same time with other metals, had to be burnt perfectly in a current of oxygen, and then reduced by hydrogen. The analysis of the cobalticyanic acid, dried at 212°, led to the formula—

$$Co^2 Cy^6 + 3H + HO.$$

The following are the results:—

Cobalt	25·80	26·17	26·25	2 =	736·88	25·96
Carbon.....	31·97	31·04	31·04	12	900·00	31·71
Hydrogen	1·99	1·99	1·94	4	50·00	1·76
Nitrogen	..	..	..	6	1051·50	37·05
Oxygen	..	..	..	1	100·00	3·52
					2838·38	

The 1 atom of water contained in the acid, dried at 212°, cannot be expelled without decomposing the acid. The amount of water in the crystallized acid could not be determined, owing to its deliquescing so readily. When dried under the air-pump over sulphuric acid, it contained the same amount of water as the acid dried at 212°. Muriatic acid dissolves cobalticyanic acid without altering it on boiling; it is scarcely soluble in concentrated nitric acid, but in greater proportion the more dilute the acid. Concentrated nitric acid, fuming nitric acid and *aqua regia* do not destroy the acid even on application of heat. It is insoluble in concentrated sulphuric acid, and is precipitated by it from a strong solution; dilute sulphuric acid readily dissolves it. When dry cobalticyanic acid is heated with concentrated sulphuric acid, it turns blue with disengagement of carbonic oxide, carbonic and sulphurous acids; and the residuary sulphuric acid contains ammonia and oxide of cobalt. If water is added to the liquid during decomposition, an amorphous, pale reddish substance is precipitated, which when heated parts with water and becomes blue, but in contact with moist air quickly reassumes its reddish colour. It is decomposed by solution of caustic potash, depositing hydrated protoxide of cobalt, and the solution contains cobalticyanide of potassium only. It is perfectly insoluble in water, and is not decomposed by concentrated muriatic and nitric acids. The following analytical results lead to the formula—

$$Co^2 Cy^6 + 3Co + HO:—$$

Cobalt	35·56	5 =	1842·2	35·81
Carbon	18·28	12	900·0	17·50
Hydrogen	3·02	12	150·0	2·92
Nitrogen	..	6	1051·5	20·44
Oxygen	..	12	1200·0	23·33

Cobalticyanide of Potassium was first prepared by L. Gmelin. According to the author, it is best obtained by dissolving protocyanide of cobalt in cyanide of potassium without the addition of any prussic acid. When the air is excluded an evolution of gas takes place, which appears to be pure hydrogen. With access of air, and likewise in oxygen, the latter is absorbed, and no disen-

gagement of gas occurs. In both cases however the liquid contains cobalticyanide of potassium and free potash. The former is obtained from it by crystallization. When much cyanide of potassium and carbonate of potash is present, the liquid is decomposed with acetic acid and precipitated with alcohol. The acetate of potash remains in solution; the cobalticyanide of potassium almost entirely separates in minute, perfectly white, shining crystals, and in a pure state. It crystallizes from its solution in water in flat, eight-sided, transparent needles, which have frequently a yellowish tint. It is insoluble in alcohol. When heated, it melts, undergoing decomposition, to a dark olive-green mass. When the air is prevented having access, cyanogen and nitrogen are given off; and on continuing the ignition, the residue contains cyanide of potassium and carburet of cobalt. When the cobalticyanide of potassium is boiled with sulphuric acid, the same phænomena occur as with the pure acid. The analysis of this salt corresponds to the formula $Co^2 Cy^6 + 3K$:—

Cobalt	..	2	=	736·88	17·74
Carbon	21·70	12		900·00	21·66
Nitrogen	..	6		1051·50	25·30
Potassium	35·80	3		1466·82	35·30

Cobalticyanide of Sodium was prepared by decomposing carbonate of soda with cobalticyanic acid; the neutralization must be very accurate, because an excess of the one or other constituent cannot well be separated by crystallization. It crystallizes in long, colourless, transparent needles, and is easily soluble in water but insoluble in alcohol. At 212° it loses the whole of its water (11·28 per cent.), and at a higher temperature behaves like the preceding salt. Its analysis led to the formula $Co^2 Cy^6 + 3Na + 4HO$.

Cobalticyanide of Ammonium was obtained by neutralizing cobalticyanic acid with ammonia, in transparent, colourless, oblique, quadrilateral prisms, which dissolve very readily in water and also somewhat in alcohol. These crystals suffer no loss in weight at 212°; at 437° they begin to be decomposed, cyanide of ammonium and carbonate of ammonia escape, and the residue becomes blue; at a still higher temperature this residue is decomposed in the same manner as the probably similar one of the pure acid. The analysis of this compound led to the formula $Co^2 Cy^6 + 3NH^4 + HO$. The ammonia in this salt was determined directly with chloride of platinum; it furnished 18·36 per cent.; calculation requires 18·23:—

Cobalt	20·92	21·68	2	=	736·88	21·19
Carbon	25·52	..	12		900·00	25·89
Hydrogen	4·54	..	13		162·50	4·67
Nitrogen	..	..	9		1577·25	45·37
Oxygen	..	..	1		100·00	2·88

Cobalticyanide of Barium was obtained by saturating carbonate of baryta with cobalticyanic acid, in colourless, transparent prisms, insoluble in alcohol but very easily soluble in water. The crystals very soon effloresce in warm air; dried at 212° they still contain

22·88 per cent. water. The formula $Co^2 Cy^6 + 3Ba + 6HO$ is calculated from the following numbers:—

Cobalt	..	2 =	736·88	12·43
Carbon	14·26	12	900·00	15·18
Hydrogen	1·40	6	75·00	1·26
Nitrogen	..	6	1051·50	17·73
Oxygen	..	6	600·00	10·13
Barium	42·81	3	2564·55	43·27

Cobalticyanide of Copper was precipitated by cobalticyanide of potassium from the sulphate of copper. The light brown amorphous precipitate is easily washed, and is then free from potash; it is consequently well adapted for the preparation of pure cobalticyanic acid. In the free state the latter likewise precipitates cobalticyanide of copper. This compound is insoluble in water and in acids; ammonia dissolves it entirely with a blue colour; potash separates the oxide of copper from it. The amount of water in the salt appears only partially to be expelled at a high temperature; at 464° the salt was bluish-green, and had lost 12·94 per cent., *i. e.* somewhat above 5 atoms of water. Its formula is $Co^2 Cy^6 + 3Cu + 7HO$.

Cobalticyanide of Copper and Ammonia crystallizes on slow evaporation of the preceding salt in minute, shining, azure-blue, four-sided prisms with eight terminal facets. Alcohol precipitates the salt in the form of a blue, slightly-crystalline powder of a much paler colour. The crystals are insoluble in water; exposed to the air and at 212°, they part with ammonia; acids remove the latter, and separate cobalticyanide of copper. When heated with solution of caustic potash, ammonia is disengaged, oxide of copper eliminated, and the solution contains cobalticyanide of potassium. On decomposition with muriatic acid, there was found 8·98 per cent. ammonia. The results of the analysis corresponded to the formula $Co^2 Cy^6 + 3Cu + 2NH^3 + 5HO$.

Cobalticyanide of Cobalt is precipitated from a solution of the protosulphate of cobalt by cobalticyanide of potassium; the free acid likewise precipitates the whole of the cobalt from solutions of the protosalt. The compound is insoluble in water and in acids; concentrated acids deprive it of water and render it blue. Solution of potash separates the hydrated protoxide of cobalt from it. At 212° the salt partially loses its water and turns blue; at a higher temperature it becomes anhydrous. Up to 428° it lost 28·93 per cent. of water, which corresponds to 14 atoms, theory requiring 29·25 per cent. according to the formula $Co^2 Cy^6 + 3Co + 14HO$. In the anhydrous state it forms an intensely blue powder, which again becomes red in moist air; when water is poured over it, it combines with it, disengaging heat. The following are the results of the analysis compared with the above formula:—

Cobalt	34·33	5 =	1842·2	34·32
Carbon	16·95	12	900·0	16·76
Hydrogen	3·59	14	175·0	3·26
Nitrogen	..	6	1051·5	19·58
Oxygen	..	14	1400·0	26·08

Cobalticyanide of Nickel can only be obtained pure by precipitating a solution of a protosalt of nickel with an excess of cobalticyanic acid. The precipitate which forms is gelatinous, pale blue, and dries in the air to a vitreous greenish-blue mass with conchoidal fracture. It is insoluble in water and in acids; at a high temperature it loses its water and becomes gray, but in contact with moist air it again reacquires it. The formula of this compound is—

$$Co^2\,Cy^6 + 3Ni + 12HO.$$

Cobalt ..... Nickel	35·43	2 = 3	736·88 1107·42	35·82
Carbon	17·49	12	900·00	17·48
Hydrogen	3·38	12	150·00	2·91
Nitrogen	..	6	1051·50	20·43
Oxygen	..	12	1200·00	23·36

Cobalticyanide of Nickel and Ammonia.—The preceding recently-precipitated gelatinous salt dissolves readily in ammonia, but that which has been dried with great difficulty. The solution is bluish, and deposits on slow evaporation cobalticyanide of nickel and ammonia. It may also be precipitated by alcohol from the solution in ammonia, and then appears at first as a white powder, and only after it has settled bluish. It is insoluble in water; acids deprive it of ammonia, and convert it into the preceding compound. In the air and at 212° it remains unaltered; when heated to redness it burns rapidly, puffing up considerably. Its composition is represented by the formula $Co^2\,Cy^6 + 3Ni + 2NH^3 + 7HO$.

Cobalticyanide of Lead.—This compound was obtained by saturating cobalticyanic acid with carbonate of lead. It crystallizes in pearly laminæ, which dissolve very readily in water, but are insoluble in alcohol. It contains 4 atoms of water, of which 4·80 per cent., or 3 atoms, go off at 212°. The formula of the salt, dried at 212°, is $Co^2\,Cy^6 + 3Pb + HO$, and that of the hydrated salt $Co^2\,Cy^6 + 3Pb + 4HO$.

Basic Cobalticyanide of Lead.—When the aqueous solution of the preceding salt is precipitated with ammonia, a voluminous white precipitate is obtained, which contains the whole of the lead; the solution contains cobalticyanide of ammonium. The precipitate is soluble in acids, but not in water; its formula is—

$$Co^2\,Cy^6 + 3Pb + 6PbO + 3HO;$$

but apparently it is not always obtained of constant composition.

Cobalticyanide of Silver is obtained by precipitating the cobalticyanide of potassium with nitrate of silver as a caseous precipitate; it is anhydrous, and not altered by exposure to light; its formula is $Co^2\,Cy^6 + 3Ag$. The following are the results of the analysis:—

Cobalt ..... Silver	70·74	2 = 3	736·88 4047·03	71·02
Carbon	13·56	12	900·00	13·36
Nitrogen	..	6	1051·50	15·62

Cobalticyanide of Silver and Ammonia.—The preceding salt dis-

solves in ammonia, and on evaporation affords colourless crystals, which are soluble in water, and when heated up to 212° lose nothing in weight; at 338° water and ammonia escape, and leave cobalticyanide of silver. This salt is represented by the formula—

$$Co^6\,Cy^6 + 3Ag + NH^3 + HO.$$

Heated to 338°, the loss of water and ammonia amounted to 4·60 per cent.

Cobalticyanic acid is, according to the facts communicated in this paper, an independent acid, which must not be regarded as a cyanogen compound in the ordinary sense. This likewise applies with respect to its action upon the animal organism. A rabbit, into whose stomach 1·16 grm. of the acid was injected, did not exhibit the least symptoms of poisoning by prussic acid. The view adopted here as to its constitution is that advanced by Liebig relative to the corresponding compounds of iron, which well explains their behaviour and their combinations.

The radical of this body = Kyc consists of the elements of 6 atoms of cyanogen and 2 of cobalt. Employing this symbol for the radical, cobalticyanic acid is Kyc + 3H + HO; it is a tribasic hydracid.—Liebig's *Annalen*, lxii. p. 157.

Experiments on the Conversion of Neutral Nitrogenous Bodies, such as Fibrine and Caseine, into Fatty Substances. By M. Blondeau.

Having had occasion to examine the manufacture of Roquefort cheese, I endeavoured to discover the alteration which the caseine experiences after it has been kept for some time in the cellars which communicate to it those qualities which render it so much sought after in commerce. Having analysed this cheese previously to its being placed in the cellars, I readily detected in it a small quantity of fatty matter; by treating it with alcohol and æther, I extracted about $\frac{1}{200}$dth of its weight of fatty matter. After having remained two months in the cellars, I found that the caseine was almost entirely converted into a fatty body presenting the greatest analogy to butter, and I was able to separate the unaltered caseine by mere boiling with water. This fatty body, which has a sweet agreeable taste, melts at 104°, begins to boil at 176°, and is decomposed at about 302°. It is easily saponified. Now under what influences has this conversion of caseine into a fatty body been effected? To answer this question, it suffices to follow for some time the course of the phænomena which take place in the cellars. There we find developed over the surface of the caseine several mycodermic plants, which grow with such rapidity that it is necessary to scrape the cheese from time to time; but nevertheless these plants reappear, and are reproduced with fresh energy. This parasitic vegetation is furthered by the humidity of the cellars, their coolness and complete darkness.

On examining these plants, I found that they consisted of several

species; first of all, *Penicillium glaucum*, the aërial stems of which cover the cheese with a long white down; then another *Penicillium*, differing from the last, and which I have named *globulosum*; two species of *Torula*, one with green sporules and called *viridis*, the other with orange-coloured sporules and called *aurantiaca*. All these vegetables contain nitrogen; their development consequently required the presence of ammonia and carbonic acid, the first to yield the nitrogen, the second the carbon. The ammonia could only be furnished by the caseine, which in parting with this alkali becomes converted into a fatty body: its composition, in fact, approaches very nearly that of the fatty bodies if we subtract ammonia. With respect to the carbonic acid, that may have been derived from the air or from the caseine.

Having once verified this conversion of caseine into a fatty matter, I was curious to examine whether on placing fibrine under the same conditions it would undergo an analogous change. I took a pound of beef free from fat, and after having slightly salted it and surrounded it with a layer of paste, I placed it in a cellar. After two months I found that this meat had undergone no putrid decomposition; but it was surrounded on all sides by the green mould, and was converted for the greater part into a fatty body presenting the greatest analogy with hog's lard. This experiment supports the view of those chemists who assert that human bodies placed under peculiar conditions, analogous to those above mentioned, may be entirely converted into a fatty body.—*Comptes Rendus*, Sept. 6, 1847.

On the Colouring Principle of Sandal Wood. By Dr. P. Bolley.

Pelletier was the first chemist who examined the colouring principle of the wood of *Pterocarpus santalinus* and made us acquainted with its preparation; he likewise published an analysis of this pigment and described some of its reactions. Subsequently Preisser published an investigation of this colouring substance in his treatise on the formation and nature of the organic pigments*. Pelletier's analysis gave 75·08 carbon and 6·37 hydrogen, which numbers approach very closely to those obtained by Prof. Johnston in his analysis of the colouring principle of dragon's blood, viz. 74·247 carbon and 6·45 hydrogen. The results obtained by the author differ from those of Pelletier; and with respect to the statements of Preisser, they are as little confirmed by this investigation as they have been in the case of most of the other pigments which have been subsequently examined.

For the preparation of the pigment the author employed,—1st, the inner pale pieces of the stem; and 2nd, a dark kind, of the colour of the wood which generally occurs in commerce. The colouring principle was obtained from the first kind in two different ways,—1st, by extracting the wood with alcohol, and precipitating the extract with water; and 2nd, by exhausting the wood with potash and precipitating with muriatic acid. This latter precipitate

* See Chem. Gaz., vol. ii. p. 371.

was then dissolved in alcohol and thrown down by water from the solution. Previously to being subjected to elementary analysis, the precipitates had to be kept for a considerable length of time at 212°, in order to remove every trace of alcohol. The following are the results obtained:—I. and II. from the alcoholic extract of the paler kind; III. and IV. from the alcoholic extract of the dark kind; V. and VI. from the alkaline extract of the pale kind, precipitated with muriatic acid and redissolved in alcohol:—

	I.	II.	III.	IV.	V.	VI.
Carbon	67·22	67·16	65·28	66·18	64·26	64·65
Hydrogen	5·67	6·02	5·55	5·43	5·27	4·88

It is seen that the carbon and hydrogen decrease in the last analysis, or that the dark kind must have been more highly oxidized, and the pale kind have absorbed oxygen during its treatment with potash. All experiments to ascertain the equivalent of the substance in its combinations with lead proved vain. The alcoholic solution of the pigment was precipitated with acetate of lead; and although the amount of lead in the precipitate could not be obtained constant, it was nevertheless analysed to ascertain the nature of the organic body in the compound. The colouring principle from the pale sample was combined with 32·18 and 31·38 per cent. oxide of lead; the same precipitate afforded on analysis 62·80 per cent. carbon, 4·74 hydrogen, and 32·46 oxygen.

According to this analysis the substance in the lead precipitate contains somewhat more oxygen than the uncombined substance. On comparing the above analytical results with one another, it appears that we may assume them to have all been formed from No. I. by the substitution of oxygen for hydrogen:—

	I.			II.		
Carbon	67·19	= 54	67·5	65·73	= 54	65·6
Hydrogen	5·84	28	5·8	5·49	26	5·2
Oxygen	26·97	16	26·6	28·78	18	29·2
	III.			IV.		
Carbon	64·45	= 54	64·67	62·80	= 54	62·93
Hydrogen	5·07	25	4·99	4·74	23	4·47
Oxygen	30·48	19	30·33	32·46	21	32·62

The properties of these four different modifications were so perfectly similar, that no perceptible distinction was evident, except that the preparation I. seemed to melt more easily than II., and this more readily than III. All three preparations did not become truly liquid when heated to 212°, but pasty. In the usual state they form amorphous resinous masses, which yield a red powder, and behave in other respects as described by Pelletier; but whence the great differences between the results of the author's analyses and those of Pelletier could not be determined; these differences are such that Pelletier's santaline cannot even be inserted in the series of the bodies above enumerated; and the assumption that a more highly oxidized

product was formed by the mode of treatment adopted by the author does not suffice to remove these differences, because the amount of hydrogen to that of the carbon in Pelletier's analysis is too small. The number of equivalents of hydrogen and oxygen in the above analyses constantly make the sum 44, which is not the case with Pelletier's results. As the changes which solutions of the sandal pigment experience by exposure to the air are a true process of putrefaction, it is useless to apply separate names to the different products. It was stated at the commencement that the author had not been able to confirm the assertions of Preisser with respect to the reduction of the sandal pigment. On treating the lead compound diffused in water with sulphuretted hydrogen and filtering the aqueous liquid, he only found traces of colouring substance when it still contained some adherent alcohol; but if it was free from alcohol, the filtered liquid was pure water; and alcohol removed the colouring principle from the precipitate on the filter.—Liebig's *Annalen*, lxii. p. 150.

On the Action of Anhydrous Phosphoric Acid upon Ammoniacal Salts. *By* M. Dumas.

In making some researches upon the effects of dehydration upon organic substances, I observed that on acting with anhydrous phosphoric acid upon crystallized acetate of ammonia, a liquid distilled over, which boiled at the fixed temperature of 171°, and mixed with water in every proportion. When purified by digestion over a saturated solution of chloride of calcium, and distilled over solid chloride of calcium and magnesia, it furnished on analysis the following numbers:—

Carbon	57·4	4	= 58·5
Hydrogen	7·4	3	7·3
Nitrogen	34·4	1	34·2

The density of the vapour was found to be 1·45.

These numbers lead to the very simple formula $C^4 H^3 N$, which differs from the acetate of ammonia in containing 4 equivs. less of water. It might be looked upon as the nitruret of acetyle $C^4 H^3$, N, or a body belonging to the type $C^4 H^3 O^3$. But the reactions of this body assign to it the rational formula $C^2 NH$, $C^2 H^2$, that is to say it is hydrocyanate of methylene or a compound isomeric with that body. The density of the vapour leads to the formula $C^4 H^5 N$, which represents 4 vols. of vapour. A boiling solution of potash disengages ammonia and regenerates acetic acid; chromic acid has no action upon it; nitric acid is not decomposed by the substance on boiling; potassium acts violently upon it in the cold, with disengagement of heat, cyanide of potassium being formed, and an inflammable gas, consisting of a mixture of carburet of hydrogen and free hydrogen.

M. Fehling obtained, on distilling benzoate of ammonia, a substance with an analogous composition to the body in question. This product is equally obtained, as we have ascertained, by the action

of anhydrous phosphoric acid. M. Fehling did not however study its reactions, nor are any theoretical views appended to the discovery of this compound. If the product which I have obtained constitutes a body identical with the hydrocyanate of methylene, all the ammoniacal salts formed by the volatile organic acids should yield, on being treated in the same manner, æthers corresponding to alcohols determined according to the general formula

$$C^n H^n O^4, NH^3 = C^n H^{n-1} N = C^{n-2} H^{n-2}, C^2 NH.$$

On decomposing the latter by potash, the alcohol $C^{n\ 2} H^{n-2}$, 2HO might be produced, and by this means the alcohols of all the fatty acids formed.—*Comptes Rendus*, Sept. 13, 1847.

On the Constituents of Lactucarium. By M. Ludwig.

The lactucone recently described by Lenoir* is, according to Walz, nothing more than the lactuca fat examined by the latter. Thieme has likewise examined the body which is removed by æther from the alcoholic extract; but he could not succeed in separating it, as stated by Walz, into a fat easily soluble in æther and one of sparing solubility in that medium, on which account he named it *lactucerine*. Ruickoldt obtained lactucerine by frequent extraction of the lactucarium with absolute alcohol, evaporation, washing the crystals so obtained with water, re-solution in absolute alcohol, again rinsing the crystals with water, and desiccation under the air-pump. The lactucarium employed by the author for the preparation of lactucerine had been collected in the neighbourhood of Ilten near Hanover. It was exhausted with water, and the insoluble residue treated several times with hot alcohol of 0·833. On the slow evaporation of the latter, a somewhat yellowish lactucerine was obtained, which was purified by washing with water, re-solution in alcohol and crystallization. The quantity of lactucerine amounted to 53·5 per cent.

Lactucerine forms snow-white aggregated granules, and dissolves in strong hot alcohol, from which it again separates on cooling; the alcoholic solution faintly reddens litmus-paper. It dissolves readily in æther, but not in water, when pure. When warmed in a platinum dish, it becomes tenacious and transparent, like turpentine; when heated more strongly, it melts completely to a clear yellow oil, gives off white vapours possessing an agreeable odour, and is volatilized with the exception of a slight residue of a perfectly-combustible cinder. Heated in a closed glass tube in a bath of chloride of zinc, it still continues pulverulent at 131° F., becomes decomposed at 158°, and disengages aromatic acid vapours at 200°. At 212° it experiences scarcely any loss; at 298° it becomes tenacious and like turpentine, without melting; at 320° it forms a thick liquid; between 356° and 374° it becomes thinner, and loses 2·110 per cent. The residue, again dissolved in spirit, separates, but still of a yellow colour. Melted at 374° in hydrogen gas, it gives off aromatic vapours, and loses 4·04 per cent. in weight. Submitted to destructive

* Chem. Gaz., p. 75 of the present volume.

distillation, it melts, becomes yellow, and gives off white vapours, which condense to a colourless liquid; subsequently a yellow oily liquid distils over, and lastly a dark oil; the residue consists of a thin coating of a shining black coal. The gases which escaped produced no turbidness in lime-water, nor could they be set light to. The distillate consisted of a colourless aqueous acid layer and a heavier yellowish-brown oil. The odour was pungent, acid and aromatic. The acid aqueous liquid gave no precipitates with oxide of mercury or silver; oxide of mercury dissolved in it without being reduced. The acid is evidently acetic acid. The oil did not dissolve entirely in alcohol, but readily in æther. Lactucerine cannot be saponified by caustic potash, but melts on evaporation to a brown mass, and is decomposed. The hydrate of sulphuric acid dissolves lactucarium immediately with a brown colour; nitric acid likewise dissolves it, and yields on evaporation a yellow residue soluble in ammonia. It gave on analysis—

Carbon....	76·202	77·286	77·090	40 =	76·650
Hydrogen..	10·654	10·832	10·902	34	10·719
Oxygen....	13·144	11·882	12·008	5	12·631

Two other experiments yielded results corresponding to the formula $C^{40}H^{33}O^4$, while Lenoir found for lactucone $C^{40}H^{31}O^3$. It appears therefore that lactucerine prepared from fresh lactucarium may be converted into lactucone by the elimination of 1–2 equivs. water. Lactucone and lactucerine are distinguished from caoutchouc, a name which has sometimes been applied to them by containing oxygen. On examining a lactucerine which consisted of microscopic crystals, the author obtained exactly the same composition for it as for the amorphous; both agreed with Lenoir's formula, having been prepared from old lactucarium.

In order to determine the other constituents of lactucarium, the author let the milk-sap ooze out of the plant into distilled water. In a few moments it separated into a bright yellow clear solution and into white floating flakes; the portion insoluble in alcohol was digested several times with æther, and this then removed by distillation. It left a waxy body, which melted at a gentle heat, and produced a permanent stain of fat upon paper. The aqueous solution of lactucarium when fresh is perfectly neutral, but becomes sour on boiling. The liquid separated from the coagulated albumen was exhausted with alcohol, and the alcoholic extract with æther:—

Lactucerine or lactucone	42·64	48·63 per cent. insoluble in water.
Waxy body, readily fusible	3·99	
Vegetable fibre, with a substance which swells in ammonia and is insoluble in water, alcohol and æther	2·00	
Albumen of a grayish colour	6·98	51·37 per cent. soluble in water.
Extract soluble in water and in spirit	27·68	
Aqueous extract, insoluble in alcohol of 0·830.	14·96	
Lactucerine, held in solution in water by the other substances	1·75	

From the bitter extract soluble in water and spirit the author obtained lactucic acid in the following manner:—80 grms. of lactucarium were rubbed to a fine powder, and then triturated in the cold with 80 grms. of pure dilute sulphuric acid, and subsequently mixed with 400 grms. of alcohol of 0·851, filtered, and the filtrate shaken with hydrate of lime until a filtered sample no longer afforded a precipitate with barytic water nor with oxalate of potash. The filtered alcoholic solution was then decolorized with pure animal charcoal and evaporated. A brown tenacious mass like turpentine separated, which dissolved in boiling water, leaving behind a tenacious viscous substance. On decolorizing the aqueous solution with animal charcoal and evaporating, a mixture of lactucic acid with Aubergier's lactucine remained; the latter separated from its solution in boiling water on cooling in white crystalline scales, and the lactucic acid was obtained on evaporation. This latter is readily soluble in water and alcohol, difficult to obtain crystallized, of a light yellow colour and strongly bitter taste; it has no acid reaction. Solution of caustic soda, lime water, barytic water and caustic ammonia colour the acid immediately, or after some time, wine-red. A solution of sulphate of copper is not precipitated by the acid; but on the addition of caustic soda and boiling, the oxide is reduced to protoxide, and the liquid acquires a dark brown colour; on adding now a little muriatic acid, brown humus-like flakes subside. There was no sugar contained in the acid, a point which was ascertained with certainty. A solution of acetate of lead gives a white precipitate; nitrate of silver is not precipitated, but on the addition of caustic ammonia and boiling, it is reduced to metal. The peracetate of iron yields with it after some time a white precipitate; concentrated sulphuric acid is coloured yellow in the cold; on the application of heat it becomes reddish-brown and black, with evolution of sulphurous acid. Concentrated nitric acid is coloured faintly yellow by it. Heated in a platinum dish, the acid melts, becomes brown, gives off acid vapours, and leaves a voluminous cinder, which is entirely consumed.

Lactucine which has been decolorized with animal charcoal and purified by recrystallization, forms white pearly scales, the solution of which exhibits no reactions with basic acetate of lead, peracetate of iron and iodine water. Concentrated sulphuric acid affords a colourless solution with it in the cold; when heated, the liquid becomes yellow, brown, and finally black. Hydrated oxide of copper is reduced to protoxide by it and the addition of potash. Lactucine melts when heated, without being coloured; at a higher temperature it becomes brown, and leaves a porous cinder, which is easily burnt.

The aqueous solution of the alcoholic extract of lactucarium, after separation of the brown mass containing the lactucic acid, left on slow evaporation a yellowish-white somewhat-crystalline mass, which, extracted with hot alcohol of 0·851, left on evaporation a neutral, insipid, sweetish body, crystallizable from water, but incapable of fermentation. The spirituous solution yielded on evaporation long silky prisms, which had all the characters of mannite.

The precipitate above obtained by agitation with hydrate of lime was supersaturated with dilute sulphuric acid; the expressed liquid was purified with animal charcoal and evaporated to a syrupy consistence. On cooling, it congealed to an amorphous gelatinous mass, of an astringent, slightly acid taste. It was extracted with water, precipitated with acetate of lead, and the precipitate decomposed with sulphuretted hydrogen. On evaporating the liquid, white prisms, which behaved precisely like oxalic acid, crystallized from it. The mother-ley contained, along with sulphuric acid, a third organic acid, which has not been further examined, but which strongly reduced solution of silver. Lactucarium, extracted with spirit containing sulphuric acid, gives up to hot alcohol much lactucerine and a soft resin, together with oxalic and lactucic acid; no sugar or gum could be detected in it. Water removed from the residue sulphate of potash, sulphate of magnesia, and basic persulphate of iron; æther took up a tenacious waxy body, which was not further examined. 3 grms. of dry lactucarium, heated in a retort for six hours in a water-bath, yielded 0·18 grm. of an aqueous colourless acid distillate, which smelt of lactucarium; on digestion with oxide of zinc it lost its acid reaction, and on evaporation its odour. 1·40 grm. of lactucarium, distilled with 3 grms. of sulphuric acid and 12 grms. water, yielded an acid distillate, which smelt strongly of lactucarium, and which, on saturation with carbonate of lime and distillation with bisulphate of potash, afforded an acid liquid, which had a valerian-like odour, and contained no acetic acid.—*Archiv der Pharm.*, l. pp. 1 and 129.

On the Composition of Uranotantalite and of the Columbite from the Ilmen Mountains. By H. Rose.

We have already enumerated the facts which led Hermann to consider ilmenic acid as the oxide of a new metal, ilmenium; and have likewise communicated his analysis of the mineral yttroilmenite in which the ilmenic acid is contained. Crystals of this mineral, sent by Hermann himself to Gustave Rose, were found by the latter to be perfectly identical with uranotantalite, formerly described by him and analysed by his brother H. Rose. G. Rose found the specific gravity of uranotantalite = 5·625; the author found the specific gravity, in a quantity received from M. Samarski of St. Petersburgh, = 5·617; and Wornum, in fragments of the same mineral, = 5·6142. Another sample, furnished by M. Afdeeff, had a higher specific gravity, viz. 5·68. With respect to the specific gravity which Hermann ascertained in different specimens of yttroilmenite, viz. 5·398–5·430 and 5·45, there is found, on comparing the properties of uranotantalite with those of yttroilmenite, an anomaly, which the author however subsequently explains. As early as 1844, while engaged in examining the various minerals containing tantalium, the author found, immediately after the discovery of niobium, that the acid obtained from the uranotantalite was a mixture of tungstic with a large quantity of niobic acid. As the red perchloride of tungsten is

far more volatile than the perchloride of niobium, they may easily be separated; and as the uranotantalite contains no pelopic acid, which it is extremely difficult to separate from niobic acid, this latter is obtained pure far more readily from uranotantalite than from the columbite of Bodenmais and North America. It is also free from perchloride of titanium. The niobic acid separated from uranotantalite, as well as the chloride of niobium, possessed all the properties which characterized the same substance procured from the columbites of North America and Bodenmais. The author observes that uranotantalite and yttroilmenite are undoubtedly identical, and that Hermann's ilmenic acid is nothing more than niobic acid contaminated with tungstic acid, and that the new metal ilmenium does consequently not exist. The author endeavours to explain the error which occurred in the following manner:—Ilmenic acid is distinguished from tantalic acid, according to Hermann, by a lower specific gravity; this is quite peculiar to a niobic acid containing tungstic acid, because of the three acids of tantalium, pelopium and niobium; that of the last metal has the lowest specific gravity, which however is somewhat raised by the admixture of tungstic acid. According to Hermann, ilmenic acid becomes yellow and blue during ignition, when the hydrate moistened with muriatic acid is placed in contact with zinc; this, as the author has formerly shown, is characteristic of niobic acid when contaminated with tungstic acid. It is further stated, that ilmenic acid expels a much larger quantity of carbonic acid than tantalic acid on ignition with carbonate of soda, which is likewise the case with niobic acid. Again, the solubility of the hydrated ilmenic acid in muriatic acid is likewise peculiar to the hydrate of niobic acid; it is only under certain circumstances that niobic acid dissolves in muriatic acid, for instance uranotantalite is entirely soluble in muriatic acid. The statement of Hermann, that ilmenic acid does not colour the fluxes before the blowpipe, the author contradicts. Niobic acid from uranotantalite colours the bead of microcosmic salt in the inner flame as blue as that from the other minerals; it only requires longer blowing, and not too small an addition of niobic acid. With respect to the brown colour which tincture of galls produces in the solution of ilmenic acid, it is also caused by a mixture of tungstic and niobic acid, the pure niobic acid from uranotantalite gives an orange-red precipitate with tincture of galls; the same applies with respect to the reaction with ferrocyanide of potassium. As regards the mineral, the name uranotantalite is at present just as inappropriate as that of yttroilmenite; it might perhaps be named uranoniobite, had not Heidinger applied the name of niobite to the Bavarian and North American columbite. The author therefore proposes to call it Samarskite.

Since the pelopic acid is replaced by oxide of uranium in samarskite, the composition of niobic, pelopic and tantalic acids is probably identical with that of the oxide of uranium. On the other hand, the yttria in samarskite appears to replace a portion of the peroxide of iron and oxide of manganese in the columbites. The columbite, which is frequently attached to the samarskite, was first discovered

by Hermann; we are now acquainted with it from three localities, from Massachussetts, Bodenmais and the Ilmen mountains. The metallic acid in the first is niobic acid with a little pelopic acid; that in the second, niobic acid with much pelopic acid; that in the last, niobic acid with traces of pelopic acid; besides which all three contain tungstic acid. The analysis of the Siberian columbite has been repeated by Bromeis in the author's laboratory; it had a specific gravity of 5·46; Hermann found 5·43–5·55. The mineral was decomposed with bisulphate of potash, and afforded 78·599 metallic acid, 12·761 protoxides of iron and manganese, 4·483 protoxide of manganese and yttria, 3·011 magnesia, 0·753 lime, 0·564 oxide of uranium, and 0·004 oxide of copper = 100·172.—Poggendorff's *Annalen*, lxxi. p. 157.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of the Protochloride of Tin. *By* Charles Nöllner.

When a long flask is filled to the top with granulated tin, and a concentrated solution of protochloride of tin is then poured into it, and kept constantly boiling, large bubbles of muriatic gas incessantly escape from the solution, which gradually dissolve the tin above the liquid; and in proportion as this happens, an amorphous crust of tin separates from the tin-solution on the surface of the liquid; so that if the boiling were continued for fourteen days, as much of the tin situated above the liquid would be dissolved as the solution previously contained. No hydrogen gas is evolved; it is merely a continuous separation and reunion of the elements of the tin-salt, the electro-negative constituents of the solution, *i. e.* the muriatic acid and the oxygen of the water combine with the tin situated above the liquid, which is there positive, and dissolve it; while the protoxide of tin and the hydrogen of the decomposed water, the positive constituents of the solution, proceed beneath the surface of the liquid to the tin, which is there negative, the hydrogen reducing the protoxide of tin, and thus eliminating tin in the form of a bright metallic layer.

If this process is carried out in the cold by placing a bar of tin in a concentrated solution of the protochloride, and carefully pouring a layer of water upon this, so that the bar of tin is situated in both liquids, we very soon observe at the place where the two liquids are in contact, the tin separate in spicula, frequently from 4 to 5 inches long. Sometimes it is also obtained in very thin quadratic laminæ, which readily separate at their centre into four rectangular triangles, and which upon closer examination under the microscope are formed exactly like those scalariform pyramids, composed of innumerable

cubes, of chloride of potassium, chloride of sodium, &c.; the spicula above-mentioned are likewise scalariform pyramids, elongated in one direction, and upon which numerous minute, very regularly formed cubes usually occur. When the separation takes place more slowly from less concentrated liquids, and especially when large quantities are operated upon, very regular four-sided columns are obtained. When, on the contrary, a solution of tin is made to support a stratum of dilute muriatic acid, or a mixture of muriatic acid and solution of tin, a stratum of water or concentrated muriatic acid and water, and a bar of tin is carefully inserted, crystals are immediately formed, but which, on account of the rapidity of their formation, resemble more closely the flowers of chloride of ammonium; just as sal-ammoniac separates on slow crystallization in cubes, but when quickly evaporated produces the well-known arborescent figures.

Above and beneath the spot where the crystals of tin separate, a thin black layer is formed, consisting of finely-divided copper with some tin when commercial tin is used, which always contains copper and some iron; when several such bars are connected, after the manner of Zamboni's battery, in adjacent glasses containing strata of tin solution and water, crystals are formed in each of the glasses; but the black deposit appears at first always in one direction, being on one side of the bar of tin above, and upon the other side below the limit where the two liquids touch; but after a time this sediment is formed both in the water and in the tin solution of each glass.

Copper resembles tin in its behaviour, but it requires from eight to fourteen days to obtain regular octahedrons.

When this electrical process is applied to the preparation of the protochloride of tin on a large scale, the ordinary plan is entirely reversed. The tin is not dissolved in dilute muriatic acid, and the saturation effected by repeatedly pouring the ley over granulated tin; but earthenware recipients, filled with granulated tin, are adapted to the retorts from which the muriatic acid is disengaged, by which a highly concentrated solution is obtained, with the advantage moreover that the muriatic acid is instantly absorbed by the tin; thus avoiding all loss of muriatic acid and its destructive effects upon the building and vegetation. Nor are the workmen at all inconvenienced by the vapours. The concentrated solution of tin is now evaporated, not in earthenware or copper vessels, but in a tin pan, which is easily constructed; and the evaporation must always be conducted as in a copper pan with a large excess of granulated tin; for even though the solution contain free muriatic acid, the granulated tin and not the pan is acted upon, the tin of the pan becoming electro-negative, while the granulated tin in the pan becomes electro-positive. All the copper contained in the liquid is deposited upon the granulated tin as a black powder, while pure tin, in bright metallic layers, is deposited upon the tin pan itself at the surface of the evaporating solution; so that if such a tin pan, after daily use for several years, should be worn into a hole, it may easily be mended by stopping it first with a tin nail, and keeping the surface of the

evaporating tin solution for a length of time at that spot, when it is gradually stopped, being as it were soldered in the *moist way*.—Liebig's *Annalen*, July 1847.

On the Estimation of the Amount of Gypsum in Culinary Salt. *By* M. Lassaigne.

To determine the amount of gypsum occurring naturally or as an adulteration in common salt, the salt is dissolved in a solution of sulphate of lime saturated at 68° F., and the residue of gypsum washed with the same liquid. In this manner the loss which would occur on edulcoration with water is avoided. 9 grms. of salt were mixed with 1 grm. of sulphate of lime, both rubbed to powder, and separated with the above liquid; 0·995 grm. gypsum was re-obtained. The method may therefore be employed in practical investigations of this kind with advantage and satisfactory accuracy.—*Journ. de Chim. Méd.*, viii., p. 425, August 1847.

Method of detecting the Adulteration of Cane-Sugar with Starch-Sugar, and the Syrup of the former with that of the latter. *By* Dr. G. Reich.

When a boiling saturated solution of bichromate of potash is added to a thick syrup of cane-sugar and the mixture heated to boiling, the chromic acid is reduced with a violent reaction, which continues even after removing the vessel from the fire, and the liquid is coloured green by the oxide of chromium in solution. When starch-sugar syrup is treated in the same manner, a very different behaviour is observed, and which may be employed to distinguish these two kinds of sugar; the starch-molasses has not the least action on the bichromate of potash; and when mixed with cane-sugar molasses to the amount of $\frac{1}{3}$–$\frac{1}{5}$, prevents the reaction of the latter; the mixture merely froths somewhat more when heated, but does not change its colour. When the amount of starch-sugar molasses is smaller, a slight alteration of colour is perceptible; but it is never so decided as with cane-sugar syrup alone. While these syrups may be thus distinguished, the sugars themselves cannot be determined in this manner, because the bichromate of potash is wholly without action upon the concentrated solutions of both, but they may be distinguished by nitrate of cobalt. When some potash is added to a concentrated solution of pure cane-sugar, and the mixture heated to boiling, a violet-blue precipitate falls, even when the solution is diluted, on the addition of a few drops of nitrate of cobalt. The dilute solution of the starch-sugar, treated in the same manner, is not precipitated; and the concentrated solution of the same sugar, to which potash has been added, deposits a dirty brown precipitate. A small amount of starch-sugar in the cane-sugar prevents the formation of the violet-blue precipitate with nitrate of cobalt. The above experiments of Reich have been repeated and confirmed by Herzog, who observes that the syrup of beet-root sugar acts as violently

on the bichromate of potash as the syrup of cane-sugar; the liquid, however, does not become green, but retains its colour like the syrup of starch-sugar. A mixture of cane-sugar syrup and the syrup of beet-root sugar must however contain far more of the latter for the green colouring produced by the cane-sugar not to appear. Herzog likewise examined the method proposed by Reich to distinguish grape-sugar and cane-sugar with nitrate of cobalt, and likewise recommends it. Beet-root sugar and mannite afford, according to Herzog, when mixed with potash, the same precipitate with solution of cobalt as cane-sugar. Milk-sugar prevents the precipitation of the nitrate of cobalt by potash, like grape-sugar. Herzog at the same time asserts that mannite, when boiled with sulphate of copper and potash, immediately reduces the oxide of copper, which is not the case according to Dr. Knop when the mannite is pure and perfectly free from grape-sugar. —*Archiv der Pharm.*, l. p. 293.

PATENTS.

Patent granted to Charles Tennant Dunlop, Glasgow, *for Improvements in the Manufacture of Alkali and Chlorine.*

The first part of this invention consists in an improved method of producing chlorine, fit for manufacturing purposes, by the mutual decomposition of the following substances:—Muriate of soda, or any other muriate; nitrate of soda, or any other nitrate; muriatic acid; nitric acid. In some instances it is also requisite to use sulphuric acid; and the patentee generally prefers to employ it in order to obtain as a residual product sulphate of soda suitable for the manufacture of soda, &c. All the above materials may be employed together, or only two of them; as, for instance, a nitrate with a muriate (in which case sulphuric acid must also be used), or a muriate with nitric acid, or a nitrate with muriatic acid, or muriatic acid with nitric acid; in the latter cases sulphuric acid is employed according to the results desired to be obtained. The patentee says he does not confine himself to any proportions, but that the process he usually adopts is to bring together common salt, nitrate of soda or nitric acid, and sulphuric acid, in suitable proportions; heat being then applied, chlorine, an oxide of azote, and muriatic acid, are evolved; these gases are caused to pass through a condenser charged with sulphuric acid, of sufficient strength to absorb the oxide of azote; and then the chlorine and muriatic acid are separated by means of water.

The second part of the invention relates to the application of the product resulting from the above process, and consists in the production of nitric acid from the sulphuric acid charged with oxide of azote, which is true nitrous sulphuric acid. This is effected by the aid of atmospheric air, steam and water; and the process adopted by the patentee is to introduce the nitrous sulphuric acid into a suitable vessel, and by the addition of water and heat to effect the disengagement of the oxide of azote, which being caused to traverse

a condenser, together with a sufficient quantity of air and steam or water, is by this means transformed into nitric acid; this acid may be again used in the manufacture of chlorine, and again recovered, and so on. Sometimes, in place of treating the nitrous sulphuric acid, as just described, the patentee causes the oxide of azote to be evolved, and to pass into a chamber into which a current of sulphuretted hydrogen is streaming, by which means sulphate of ammonia is obtained and sulphur deposited.—Sealed March 16, 1847.

Patent granted to James Napier, Middlesex, *for Improvements in smelting Copper and other Ores.*

This invention consists in improvements in smelting copper ores, by treating them with fluxes consisting of common salt, lime and carbonaceous matters; and also in improvements in smelting ores containing silver or gold, or both those metals, by the addition of alkaline substances, coal, iron and galena.

The first object is to facilitate the separation of the earth from the copper; and to effect this, when several ores of different descriptions are to be operated upon, the patentee mixes them in such proportions, in relation to the earthy matters or gangue they contain, as will cause the earths to unite in the furnace and form glass; the ores have been mixed in suitable proportions, when the silica in the mixture ranges from 50 to 75 per cent., in relation to the other earthy matters, which are generally mixtures of alumina, lime, baryta, fluor-spar, &c.; the presence of oxide of iron greatly facilitates the fusion of the ores. Should the mixture (or the ore, when only one description of ore is being treated) not contain silica in the above proportion, the deficiency is to be supplied by the addition of sand; or if the silica exceeds the above proportion, lime or fluor-spar is to be added.

After the above preparatory process, the operation is conducted in the following manner:—If the ore or ores should contain not less than 1 part of iron and 1 part of sulphur to 2 parts of copper, an addition is made to every ton of the ore of 56 lbs. common salt, 40 lbs. of slaked lime, and 100 lbs. of coal, and the whole is fused in a melting furnace. When fused, the slag or scoria is skimmed off, and the furnace is tapped into sand moulds. The ingots or pigs thus produced are treated as hereafter described. If the ore or ores should contain less than 1 part of iron to 2 parts of copper, the deficiency is to be supplied by the addition of sulphuret of iron; or the ore is to be treated as before mentioned (omitting the coal); and after the fused mass has been skimmed, 30 lbs. of scrap iron are to be dispersed over the surface thereof as equally as possible, and the door of the furnace is closed until the scrap iron is melted; the furnace is then to be tapped into sand moulds. When the ingots obtained in the above manner are set, they are thrown into water, whereby they become disintegrated and fall into a fine powder; this powder is thrown into a heap, and allowed to remain for forty-eight hours; after which it is removed to a calcining furnace,

and treated in the manner described in the specification of a patent obtained by the present patentee, July 20, 1846*. The addition of black oxide of manganese, instead of iron, has been found to produce a similar effect, but not with equal advantage.

When ores containing little or no sulphur are operated upon, the above-mentioned processes of disintegration and calcination are omitted. The patentee commences, in this case, by mixing the ores in relation to their earthy matters so as to form glass, as above described (the ores, when containing no iron, might with advantage have a small quantity of oxide or carbonate of iron added); and then 80 lbs. common salt, 50 lbs. slaked lime, and 100 lbs. anthracite coal, finely pulverized, are added to each ton of ore containing 10 per cent. of copper. If the ore should be richer in copper, a smaller proportion of salt and lime will suffice, and a greater proportion of anthracite coal will be required. The patentee says he has found that for an ore containing 25 per cent. of copper, 56 lbs. common salt, 50 lbs. slaked lime and 150 lbs. anthracite coal will answer well. The mixture of ore and other materials is fused in a melting furnace, which for a charge of 25 cwt. of ore will take from five to six hours; and then the fused mass is tapped into sand moulds. The copper thus obtained will generally be ready for the refining operation; but should a portion of the produce be regulus, it is to be roasted, and afterwards refined. Soda and several of its salts may be used instead of common salt; and so likewise may potash and several of its salts, or mixtures of these, free from sulphur.

Sulphuretted ores of copper, containing silver or gold, or both these metals, are treated in the following manner:—The ore is first calcined and fused, as in the ordinary smelting process, so as to produce a regulus containing about 50 per cent. of copper; with every ton of this regulus, 56 lbs. soda-ash, 40 lbs. slaked lime, 1 cwt. coal, $1\frac{1}{2}$ cwt. iron in scraps and 4 cwts. galena (sulphuret of lead) are mixed, and the mixture is fused in a fusing furnace until the iron disappears; the fused mass is then well rabbled, and tapped into sand moulds. The lead will be found reduced at the bottom of the first and second ingots, and will contain all, or the greater part, of the silver or gold, or both, which the ore previously contained; these metals are afterwards separated from the lead by the ordinary methods of separating silver and gold from lead. The copper is treated in the ordinary manner, or as described in the specification of the patent before alluded to. Instead of galena the oxide of lead may be employed, in which case the iron is dispensed with; but the patentee prefers to use galena.

When treating ores of silver or gold, or both, which do not contain copper, or which do not contain it in the state of a sulphuret, the patentee adds copper pyrites thereto, in the proportion of 4 cwts. of the latter to 16 cwts. of ore, and then proceeds in the manner above described, viz. bringing the material into a state of regulus, and fusing it with soda-ash, lime, coal, iron and galena.—Sealed March 2, 1847.

* For description of this invention see page 127 of the present volume.

THE CHEMICAL GAZETTE.

No. CXXII.—November 15, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Red Colouring Principle of Anchusa tinctoria.
By Drs. Bolley *and* Wydler.

The red colouring principle of the so-called alkanet-root has been already examined by Pelletier and John, and both agree that its solutions are altered by boiling. It is moreover known to every dyer that the pigment of this root is so changed by light that its solution very soon becomes unfit for use. In the following experiments, which were made with a view to obtain some explanation respecting the metamorphosis of this body, the roots were first exhausted with cold water, which removed a brown matter; the water had a slightly acid reaction and a bitter taste, and left on evaporation a brown extract; it also exhibited very distinctly the reactions of tannic acid. The roots were then dried at a gentle heat and exhausted with alcohol; but on distilling off the alcohol, the red colour was changed into a violet, and subsequently into a greenish-gray one, as described by Pelletier and John. The authors observed that this destruction of the pigment on evaporation might be prevented by a small addition of muriatic acid; and recommend this process to dyers, in order to preserve solutions of the colouring principle for a longer time, and for the purpose of concentrating dilute solutions. The solution in alcohol, to which muriatic acid had been added, was evaporated until the whole of the alcohol had been removed, and the thick residuary liquid, turbid from the separation of pigment, was agitated with æther, which became dark red. The solution in æther was mixed with water and frequently shaken; the æthereal liquid floated on the top, and after removing the acid reddish-brown water was repeatedly agitated with fresh water until the æthereal liquid had diminished and become quite thick; this on evaporation left a dark red, brittle, resinous mass, which possessed in general the properties mentioned by Pelletier, only that it was found to be perfectly neutral and not acid, as stated by him. Alkalies colour the alcoholic solution blue; acids precipitate brown-red flakes from the solution. A spirituous solution of perchloride of tin produces a violet colouring, but no precipitate, as stated by John. Perchloride of iron produces a very slight precipitate, but colours the solution dark olive-green. An alcoholic solution of neutral acetate of lead produces no precipitate;

one of the basic salt gives a bluish-gray precipitate. But this lead precipitate is tolerably soluble in alcohol, for the tincture cannot be decolorized by a large excess of the basic acetate; and when it is washed with alcohol, it constantly alters its composition, and the latter distinctly exhibits the reaction of lead. It was attempted to reduce this lead precipitate according to the general method proposed by Preisser, by means of sulphuretted hydrogen; but again in this case it led to a negative result. As the acid reaction which Pelletier ascribed to this substance is not peculiar to it, the name Anchusic acid must be changed into *Alkanet-red* or *Anchusine*. The following analyses were made with chromate of lead:—

Carbon	71·33	35 =	71·44
Hydrogen	7·00	20	6·80
Oxygen	21·67	8	21·76

The amount of lead in the precipitates varied between 50 and 77 per cent., so that the determination of the atomic weight by means of this compound could not be made. Pelletier found in one analysis of this same pigment 71·178 carbon, 6·826 hydrogen, and 21·996 oxygen; and thence calculated the formula $C^{17}H^{10}O^4$, which, according to the greater amount of carbon found, must be changed into the one above given.

On distilling the alcoholic solution of the colouring principle, without the addition of muriatic acid, it is decomposed into a substance which dissolves in æther with a green colour, and one which is soluble in water with a brown colour. After sufficiently boiling the alcoholic solution, and evaporating it to dryness in the water-bath, the mixture of the two substances remains as a blackish-green mass, from which the brown matter is extracted with water. The green substance, *Alkanet-green*, is sparingly soluble in alcohol, but very easily soluble in æther; dilute solution of caustic potash takes up a little with a greenish colour, and muriatic acid precipitates the organic body from this solution in brownish flakes. On analysis it yielded the following results:—

Carbon	69·81	70·35	34 =	70·34
Hydrogen	7·69	7·52	22	7·64
Oxygen	22·50	22·13	8	22·06

The formation of this green substance from the red is explained in the following manner:—

$$C^{35}H^{20}O^8 + 2HO = C^{34}H^{22}O^8 + CO^2,$$

according to which the elements of 2 atoms of water have been assimilated and 1 atom of carbonic acid set free. As no nitrogen had been found in the red colouring principle by Pelletier nor by the authors, the products resulting from its decomposition were at first not more closely examined; but the authors soon found that the brown substance contained nitrogen. The wash-water of the above solution of the red pigment, the brown substance into which the red pigment is decomposed on boiling its alcoholic solution, and lastly the brown extract removed from the root at the very outset by means of water, all contained ammonia. This ammonia is the cause

of the decomposition of the red pigment into alkanet-green and the brown substance; for the red principle, evaporated with muriatic acid and redissolved in alcohol, could be boiled for more than four hours without altering its colour, while a small addition of the brown aqueous ammoniacal extract, or of free ammonia, very soon produced the change of colour.

The brown substance possesses the following properties:—It dissolves readily in water, but is insoluble in æther and strong alcohol; alkalies colour the solutions somewhat darker. The solution precipitates several metallic salts, and on slow evaporation with access of air it acquires a very acid reaction. According to the following analysis its composition may by expressed by $C^{29}H^{15}O^{28} + NH^4O$:—

Carbon	40·05	29 =	39·61
Hydrogen	4·32	19	4·55
Nitrogen	3·12	1	3·19
Oxygen	52·51	29	52·84

This body, which probably belongs to the series of the humus-like substances, is certainly the same which the water had extracted from the root. Whether it be a product of decomposition of the red pigment or not is left uncertain.—*Ann. der Chem. und Pharm.*, lxii. p. 141.

Further Researches on the Action of Anhydrous Phosphoric Acid upon Ammoniacal Salts. *By* Messrs. Dumas, Malaguti and Leblanc.

The authors have examined the action of anhydrous phosphoric acid upon the butyrate and the valerianate of ammonia, when analogous bodies to that yielded under the same circumstances by the acetate of ammonia are formed. Thus all these products act in the same manner upon potassium, giving rise to cyanide of potassium and to a mixture of hydrogen and carburetted hydrogen, the condensation of which increases in proportion as the acid from whence it is derived is removed from acetic acid. All these bodies, under the influence of potash, fix water, liberate ammonia, and regenerate the acid of the primitive salt.

The chloracetate of ammonia, a salt of the same type as the acetate, furnished reactions which were perfectly in accordance with the analogous chemical properties which connect acetic acid with chloracetic acid. Thus acetate of ammonia furnishes the body C^4H^3N, and the chloracetate of ammonia yields with anhydrous phosphoric acid the substance C^4Cl^3N. This last substance is liquid with the specific gravity of 1·444, and boiling at 178°; its equivalent, expressed by the above formula, represents 4 vols. of vapour. It yields chloroacetic acid under the same conditions that the hydrogen compound C^4H^3N furnishes acetic acid; it is violently acted upon by potassium, but the authors have not yet determined the nature of the products.

Chloracetamide, a body belonging to the acetic series, exhibited

the same behaviour as the chloracetate of ammonia when treated with anhydrous phosphoric acid, which leads the authors to presume that the amides may be substituted for the ammoniacal salts in investigating this class of reactions. It is known in fact that the amides differ from the ammoniacal salts only by containing 2 equivs. less of water. If it be borne in mind that oxalate of ammonia and oxamide, and on the other hand the formiate of ammonia, may, by parting with their water, give rise to cyanogen and to hydrocyanic acid, the facts and new class of experiments above described afford arguments in favour of relations expressed by the following formulæ:—

Oxalate of ammonia ..	C^2O^3,NH^4O	$-4HO=C^2N$
Formiate of ammonia..	C^2HO^3,NH^4O	$-4HO=C^2N,H$
Acetate of ammonia ..	$C^4H^3O^3,NH^4O$	$-4HO=C^2N,H+C^2H^2$
Butyrate of ammonia ..	$C^8H^7O^3,NH^4O$	$-4HO=C^2N,H+C^6H^6$
Valerianate of ammonia	$C^{10}H^9O^3,NH^4O$	$-4HO=C^2N,H+C^8H^8$

Comptes Rendus, Sept. 27, 1847.

On the Constitution of Cyanuric Acid. By Prof. Wöhler.

The examination of some salts of cyanuric acid has led the author to a new view respecting the constitution of this acid. Liebig assigned to it the formula $3HO + C^6N^3O^3$, in which the 3 equivs. of water are looked upon as capable of being replaced by bases. According to Wöhler, the effloresced acid should be expressed by $2HO + C^6HN^3O^4$; it is bibasic, and contains 1 equiv. of hydrogen, not in the state of water, but belonging to the constitution of the anhydrous acid with 4 equivs. oxygen. In this form the composition of the acid stands in a remarkable relation to that of urea. The formula of the acid supposed anhydrous $C^6N^3HO^4$ may be split into $2C^2NO$ and C^2NHO^2, or into 2 atoms of cyanic acid and that body which Berzelius calls oxide of urene, and which according to his view constitutes urea when conjoined with 1 equiv. ammonia. Wöhler is very much inclined in favour of Berzelius's view, that all organic bases are conjugate ammonia compounds; he at the same time views cyanuric acid as a conjugate cyanic acid, which takes up 2 equivs. of base, because it contains 2 atoms of cyanic acid in its equivalent. The conjunct C^2HNO^2 is combined with 1 equiv. hydrated cyanic acid $HO + C^2NO$, and is isomeric with the body which Wöhler and Liebig formerly called insoluble cyanuric acid, but is not identical with either of the two substances. The view here entertained respecting the constitution of this acid and its salts is proved by what follows.

Neutral cyanurate of Silver, $2AgO + C^6N^3HO^4$, is a colourless crystalline powder, which is insoluble in water, and does not blacken by exposure to the light. With a magnifying power of 200 it is seen to consist of rhombohedral crystals. At 392° it loses nothing in weight and does not alter its colour; at a higher temperature it first becomes cinnamon-brown, subsequently disengages an odour

of cyanic acid, and burns to metallic silver. In hydrogen it is reduced at 212° to the violet-black protosalt. The salt is obtained by adding recently-precipitated carbonate of silver to a boiling hot solution of cyanuric acid, leaving a little of the latter unsaturated; or by dropping a boiling solution of cyanuric acid mixed with acetate of soda into a dilute boiling solution of nitrate of silver, taking care to have an excess of the latter; or by pouring a boiling solution of cyanurate of ammonia into a boiling solution of nitrate of silver, preserving an excess of the latter. The safest plan however is to mix a hot solution of cyanuric acid with a hot solution of acetate of silver. Free acetic acid does not decompose the cyanurate of silver. On analysis the following results were obtained:—

					Calculated.
Silver	62·48	63·54	62·56	62·70	62·95
Carbon.....	10·62	..	..	..	10·51
Hydrogen....	0·34	..	..	..	0·29

Cyanurate of Silver and Ammonia, $2AgO + C^6 N^3 HO^4 + 2NH^3$, is formed when the preceding salt is digested with ammonia; it does not dissolve in it, but alters in appearance. At 140° it parts with ammonia, which is wholly expelled between 392° and 572°. The salt dried at 68° gave 57·05 per cent. silver; the above formula requires 57·27.

Cyanurate of Silver and Potash.—Cyanurate of silver is not decomposed by a boiling solution of caustic potash; but the salt combines with potash, which cannot be removed by washing.

Tribasic cyanurate of Silver.—A boiling solution of cyanuric acid, to which an excess of ammonia had been added, was gradually precipitated, according to Liebig's direction, by nitrate of silver; an abundant pulverulent precipitate formed, which was boiled for a quarter of an hour with the ammoniacal liquid. This was then filtered boiling, and the precipitate washed with hot water; it appears to be homogeneous, and to consist of minute prisms with a magnifying power of 200. When potash is poured over it, it disengages ammonia, and also when heated alone; at a high temperature it is decomposed with a hissing noise, leaving a residue of metallic silver. Dried at 212°, it afforded 68·52 per cent. silver; but dried at 392°, 70·20; and at 572°, 70·55. On burning it with oxide of copper, 8·401 carbon and 1·35 hydrogen were obtained. These numbers agree well with those found by Liebig in his analysis of the heated salt. At all events, the salt contains 3 equivs. silver to 6 atoms of carbon or to 1 equiv. cyanuric acid; but it likewise contains hydrogen as an essential element, and must therefore be expressed by the formula $3AgO + C^6 HN^3 O^4$. The following numbers allow of a comparison being made between the results obtained by Liebig and Wöhler and those calculated according to Wöhler's formula:—

	Liebig.		Wöhler.		Calculated.
Silver	70·00	71·10	70·200	70·55	70·570
Carbon....	8·13	7·81	8·400	..	7·850
Hydrogen..	0·13	0·08	0·135	..	0·217

Cyanurate of Silver and Oxide of Ammonium is deposited from the liquid filtered from the preceding salt as a white powder in large quantity on cooling. It was washed and dried at the ordinary temperature. It consisted of delicate, long, microscopic prisms, disengaged ammonia even below 212°, and lost after two hours' heating up to 482° 7·0 per cent. in weight, remaining perfectly white. It left on ignition 53·33 per cent. silver. The same salt is obtained when a hot solution of nitrate of silver is added to a hot solution of crystallized cyanurate of ammonia, and the precipitate which forms is boiled with the liquid. It is very probably a double salt of cyanurate of ammonia with cyanurate of silver

$$= 3AgO + C^6 HN^3 O^4 + 3NH^4 O, C^6 NH^3 O^4.$$

If it were composed according to this formula, it should yield 49·9 per cent. silver when dried at the ordinary temperature; one experiment gave 49·4. At 482°, 2 equivs. ammonia and 1 equiv. water might escape, and the residue consist of

$$3AgO, C^6 H N^3 O^4 + NH^4 O, HO + C^6 HN^3 O^4.$$

The heated salt should then leave 53·53 per cent. silver; experiment gave 53·33. Besides this there is at least another double salt of silver and ammonium.

Cyanurate of Lead.—A salt with less than 3 atoms of lead could not be obtained. A solution of acetate of lead, rendered acid with acetic acid, is not precipitated by cyanuric acid. The salts prepared by the following methods have constantly the composition $3PbO + C^6 HN^3 O^4 + 2HO$. When acetate of lead is mixed with cyanurate of ammonia, or a boiling solution of cyanuric acid is imperfectly saturated with carbonate of lead, or basic acetate of lead is added to a boiling solution of cyanuric acid, with the precaution that some free cyanuric acid remain in the solution, this compound is obtained in the form of a heavy crystalline precipitate, consisting of well-defined, transparent, microscopic prisms, with very obtuse terminal faces. When heated in hydrogen, a large quantity of cyanide of ammonium and urea is formed, and the residue is pure lead. This behaviour was taken advantage of in the analysis of the salt, in order to obtain more accordant results than by burning the lead-salt. At 392° it begins to part with water. The 2 atoms of water which it contains amount to 3·88 per cent. At 482° it had lost exactly the half; the second atom of water is only expelled at a temperature at which the salt is decomposed. On burning with oxide of copper, 5·57 and 5·70 per cent. water were obtained, in which is contained the hydrogen of the acid. According to the above formula it should yield 5·71. The analyses of the salt, dried at 212°, yielded—

				Calculated.
Oxide of lead	72·32	72·40	72·53	72·17
Carbon	7·98	8·00	7·89	7·77
Hydrogen.....	0·63	0·62	..	0·64

On reducing this salt to a very fine powder, and boiling it with a large excess of nitrate of silver until it had entirely altered its ap-

pearance, a salt was obtained in which 2 atoms of lead were replaced by silver, according to the formula

$$2AgO, PbO + C^6 HN^3 O^4 + HO.$$

After desiccation at 212° and reduction in hydrogen, it furnished 69·64 per cent. of metal, of which 45·94 parts were silver.

Cyanurates of Copper.—No neutral copper-salt has hitherto been prepared. On mixing cyanurate of ammonia with salts of copper, the precipitates were constantly contaminated with the copper-salt; but on mixing a very dilute solution of cyanuric acid in warm ammonia with an equally dilute solution of sulphate of copper in ammonia, a very beautiful violet salt separated on cooling in minute crystals. It is so insoluble in water, that it can be perfectly washed with it.

When magnified, the crystals appeared as amethyst four-sided prisms. This salt is scarcely soluble in ammonia, is not altered by exposure to the air, and begins to disengage ammonia at about 212°. Heated to 446°, it becomes of a dark olive-green, losing 14·85 per cent. in weight without the crystals falling to pieces; at a higher temperature it becomes pale yellow, then takes fire, and burns to oxide of copper. It contained no sulphate. The salt, dried at 86°, gave 32·850 per cent. oxide of copper; that heated to 446° afforded 38·59 per cent. oxide of copper, 13·28 ammonia, 14·798 carbon, and 3·944 hydrogen; the salt evidently consists therefore of

$$2CuO, C^6 HN^3 O^4 + 2NH^3 + 3HO;$$

according to which it should yield 31·50 oxide of copper, 13·50 ammonia, 14·30 carbon, and 3·57 hydrogen. This salt is probably the cyanurate of ammonia and copper,

$$2CuO, NH^4 O + C^6 HN^3 O + NH^3, 2HO;$$

and the olive-green salt, produced at 446°, the oxide of ammonium-salt free from ammonia and anhydrous,

$$= 2CuO\,NH^4 O + C^6 HN^3 O^4.$$

Several other salts of this class exist.

Cyanurate of Baryta is formed when barytic water is added to a boiling solution of cyanuric acid until the precipitate, which at first redissolves, begins to be constant, which is indicated by a pulverulent turbidness; the liquid is subsequently kept for several hours at 140°, in order that no free cyanuric acid may be deposited. In this interval a very crystalline precipitate separates, which is filtered from the liquid while hot. Chloride of barium and acetate of baryta are not precipitated by free cyanuric acid. The salt forms transparent prisms, which begin to lose water at 392°, but do not part with the whole until 536°, when they appear of a milky-white colour. The analyses of the salt, dried at 212°, lead to the formula

$$BaO + C^6 HN^3 O^4 + 3HO:—$$

				Calculated.
Baryta	35·34	35·48	35·57	35·63
Water	8·45	8·45	..	8·38

Of the 3 atoms of water, only 2, or 8·38 per cent., escape at 536°.

At a higher temperature the acid is decomposed. This salt must be viewed as an acid salt,

$$2BaO\ C^6\ HN^3\ O^4 + 2HO,\ C^6\ HN^3\ O^4 + 4HO,$$

which 4 atoms of water escape at 536°. The neutral salt is obtained as a crystalline precipitate when a boiling solution of cyanuric acid is mixed with chloride of barium and then with ammonia, or when the solution of cyanuric acid is poured into an excess of baryta water. It is easily contaminated with carbonate of baryta and the preceding salt. At 392° it begins to part with water; kept for some time at 482° it loses 6·45 per cent. water. At a higher temperature it disengages ammonia, cyanic acid, and lastly melts to neutral cyanate of baryta. The analyses of the salt, dried at 212°, furnished—

			Calculated.
Baryta	53·38	52·90	52·56
Water	14·04	13·39	13·27
Water of crystallization	6·45	..	6·15 at 482°

according to which the salt is $2BaO, C^6\ NH^3\ O^4 + 3HO$. Of the 3 equivs. of water only 2 can be expelled by heat.

Cyanurate of Potash.—The sparingly soluble potash-salt, which according to Liebig's view is $KO, 2HO + C^6\ N^3\ O^3$, is according to Wöhler $KO + C^6\ HN^3\ O^4 + HO$; and the second easily soluble salt, which Liebig represents by the formula $2KO, HO + C^6\ H^3\ O^3$, must according to Wöhler be expressed by $2KO + C^6\ N^3\ HO^4$.—*Annalen*, lxii. p. 241.

On a new Chlorinated Compound derived from the Dutch Liquid. *By* I. Pierre.

This new compound, which is represented by the formula $C^4\ HCl^5$, fills up the gap in the chlorinated series derived from the Dutch liquid. It afforded on analysis—

				Calculated.
Carbon	..	..	11·75	11·87
Hydrogen	..	..	0·60	0·49
Chlorine	87·71	87·46	..	87·64

This body is obtained without any difficulty by the action of chlorine on the Dutch liquid. Like all the compounds of the same series, this body loses in the presence of an alcoholic solution of potash the elements of 1 equiv. of hydrochloric acid, and gives rise to a deposit of chloride of potassium. But while the former yield very readily decomposable compounds, this gives rise to protochloride of carbon, $C^4\ Cl^4$, which is very stable. The reaction is extremely violent, instantaneous, and accompanied by a considerable disengagement of heat; it may be expressed by the following equation:—

$$C^4\ HCl^5 + KO = C^4\ Cl^4 + KCl + HO.$$

This substance is liquid even at 32°; it boils at 309° F. Its specific gravity at 32° is 1·66; its odour is agreeable, somewhat like honey; it has a sweet hot taste, but much less so than that of the

Dutch liquid itself. The specific gravity of its vapour at 407° is 7·087. Admitting that the formula $C^4 HCl^5$ represents 4 vols. of vapour, we find by theory the number 7·101.—*Comptes Rendus*, Sept. 20, 1847.

Observations on Nicotine. By M. Barral.

The formula $C^{10} H^8 N$, advanced by Barral and Ortigosa for nicotine, was subsequently altered to $C^{10} H^7 N$ by Melsens and Schlœsing. From the known properties of this body, Schlœsing has suggested that the above formula should be doubled. But since all the salts of nicotine are deliquescent, they cannot serve to determine the atomic weight with certainty; and the double salts of nicotine with platinum and mercury leave the question undecided, as they may be explained in favour both of the simple and of the doubled formula.

This induced the author to take the density of the vapour of nicotine, and as its composition approaches so closely to that of aniline, that of the latter likewise, in order to render the formulæ thence deduced comparable with each other. The determinations of the density of the vapour of nicotine gave as the specific gravity of the vapour 5·630 and 5·607. Taking these numbers as a basis, calculation according to the formula $C^{10} H^7 N$ leads to 2 vols. of vapour. The density of the vapour of aniline was found to be 3·21, according to which the formula of aniline $C^{10} H^7 N$ contains 4 vols. of vapour. Since the formula of ammonia must be expressed by 4 vols. gas, and ammonia and aniline possess an equal volume, it is probable that the formula of nicotine likewise contains 4 vols. vapour, and that the formula should in fact be doubled, viz. $C^{20} H^{14} N^2$. This causes most of the analogies between nicotine and aniline, upon which some chemists have built sundry hypotheses with respect to the artificial preparation of nicotine, deriving it from already known and unknown compounds, to disappear. The specific gravity of nicotine is at—

39° = 1·033, 59° = 1·027, 86° = 1·018, 122° = 1·0006, 215° = 0·9424.

Aniline dissolves phosphorus and sulphur, nicotine only the latter. At 212° 100 parts of nicotine dissolve 10·58 sulphur, which separates for the greater part on cooling in acicular crystals. Nicotine absorbs from moist atmosphere nearly twice its weight of water, which it again completely loses in air dried over potash. Nicotine with a certain amount of water solidifies when cooled by a mixture of ice and common salt, which the anhydrous does not. Chlorine acts violently upon nicotine. When a few drops are allowed to fall into a flask filled with chlorine, the reaction is so powerful as sometimes to produce fire, muriatic acid is disengaged, and a blood-red liquid obtained, which is decolorized in sunlight, and is converted below 47° into acicular crystals; the latter again deliquesce as soon as the temperature rises above 47°. When this product is treated with water it is decomposed, and a white body separates, which may

be obtained in a crystalline state from alcohol. After the separation of this body the water has an acid reaction.—*Ann. de Chim. et de Phys.*, xx. p. 345.

Researches on Gentianine. *By* Dr. Baumert.

Gentianine was first considered to be the bitter and medicinal principle of the gentian root; and subsequently, after it had been prepared by Tromsdorff pure and free from the bitter principle of the root, it was looked upon as a colouring substance, and called by Lecomte *genticine*. The following investigation makes us acquainted with the composition and chemical nature of this body. To prepare it, the gentian root was first freed from a portion of the bitter extract by exhaustion with cold water, then dried again and extracted with alcohol. On removing this by distillation, a brown resinous mass, of an excessively bitter taste and acid reaction, remains. On pouring water over it, light brown flakes separate, while the bitter principle, the acid, sugar, &c., dissolve in the water. The precipitate thrown down by water from the syrupy residue is purified as much as possible from the bitter substance by washing; it then contains gentianine, a caoutchouc-like substance, fat, and still some of the bitter principle. The fat is removed by treatment with æther, and the residue again dissolved in strong alcohol, which upon evaporation leaves a crystalline mass still possessing a bitter taste and containing an admixture of resin. The gentianine is at last obtained pure by frequent recrystallization in light yellow acicular crystals; but this mode of preparation is connected with considerable loss, as the gentianine is somewhat soluble in water, and still more so in æther. Only 1 drm. of gentianine was obtained from 20 lbs. of the root; but even this amount was greater than that obtained according to the process advised by Lecomte, which is based upon the fact that the gentianine is not precipitated by the neutral acetate, but only by the basic acetate of lead, so that a great portion of the impurities can be removed by a solution of the first salt.

Gentianine crystallizes in slender, pale yellow, tasteless needles. It is very sparingly soluble in water; 1 part requires 3630 parts water; it dissolves best in boiling alcohol; it dissolves in alkaline water, imparting to it an intense yellow colour; it is permanent in the air, and may be heated to 392° without loss of water; it sublimes between 572° and 644°, disengaging yellow vapours, which condense into fine needles, while the greater portion is carbonized with evolution of a peculiar odour. Gentianine has the following composition:—

Carbon	65·05	65·09	65·04	14 =	1050·0	65·11
Hydrogen	4·15	4·24	4·10	5	62·5	3·87
Oxygen	30·80	30·67	30·86	5	500·0	31·02
					1612·5	

Gentianine has no reaction upon the vegetable colours; it is a neutral or indifferent body, which combines with acids and bases

without parting with the elements of water. It expels carbonic acid from the carbonated alkalies, but the carbonic acid of the atmosphere likewise decomposes several of its combinations if they are still moist.

Gentianine and Soda.—The combinations of gentianine with soda may in general be easily obtained in a crystalline state, and are of a yellow colour. They have an alkaline reaction; those containing water effloresce; they are more soluble in water than pure gentianine; but a large addition of water separates the gentianine in flakes, while the soda rapidly absorbs carbonic acid. The soda compounds are likewise soluble in alcohol; but on each recrystallization from alcohol they contain less soda, until at last pure gentianine is left. $NaO + 3C^{14} H^5 O^5$ is obtained by exhausting gentianine and carbonate of soda with alcohol of 0·833 until nothing further dissolves; the crystals which separate from the liquid on cooling were once recrystallized from absolute alcohol. They yielded on analysis the atomic weight 5373, and—

Carbon.....	59·60	42 =	3150·0	60·25
Hydrogen	3·88	15	187·5	3·67
Oxygen	29·25	15	1500·0	28·61
Soda.....	7·27	1	390·9	7·47
			5228·4	

$NaO, 2C^{14} H^5 O^5 + 8HO$ was obtained by adding an aqueous solution of carbonate of soda to the solution of the preceding salt without separating gentianine, and the mass evaporated to dryness; the residue was exhausted with absolute alcohol, and the crystals obtained from this solution recrystallized. They contain water and effloresce; on desiccation at 212° their golden colour changes into a brown. The atomic weight found was 3571; elementary analysis gave—

Carbon.....	58·04	28 =	2100·0	58·08
Hydrogen	3·72	10	125·0	3·45
Oxygen	27·30	10	1000·0	27·66
Soda.....	10·94	1	390·0	10·81

The hydrated salt yielded 20·14–20·18 per cent. water; calculation, according to the formula with 8 atoms of water, requires 19·93. The same compound is formed when gentianine is evaporated to dryness with solution of caustic soda, and the residue exhausted with absolute alcohol; for the atomic weight found for a salt obtained in this manner was 3615, which agrees accurately with the calculation; it also contained 20·14 per cent., *i. e.* 8 atoms of water.

$NaO, 6C^{14} H^5 O^5 + HO$.—This compound was procured by mixing an alcoholic solution of gentianine with an aqueous solution of carbonate of soda without separating gentianine, evaporating to dryness, and exhausting the residue with alcohol. The salt was obtained in crystals resembling in general the previous compounds. They contain, moreover, 10·12 per cent. water, corresponding to the formula with 1 atom of water. Several other compounds of gentianine with soda exist, which may be obtained by varying the

above process. All those examined contained the gentianine in a multiple of $C^{14} H^5 O^5$, and no compound could be prepared containing 1 atom of $C^{14} H^5 O^5$ to 1 atom of soda.

Gentianine and Potash.—These compounds very much resemble those with soda; the author obtained $KO + 4C^{14} H^5 O^5 + 3HO$ in golden stellately-grouped needles, $2KO + 5C^{14} H^5 O^5$ with 16 atoms of water of crystallization, and $KO + 2C^{14} H^5 O^5 + 5HO$. Notwithstanding the variety of the compounds of potash with gentianine, no salt could be prepared containing the simple formula $C^{14} H^5 O^5$.

Gentianine and Baryta.—The neutral compound $BaO + O^{14} H^5 O^5$ is obtained by mixing the alcoholic solution of gentianine with barytic water as an orange flocculent precipitate, which on drying shrinks very much, and only re-acquires its primitive colour on pulverization. So long as it is not perfectly dry, it rapidly absorbs carbonic acid from the air, and then contains an admixture of carbonate of baryta; it must therefore be quickly washed and dried. The analysis was made with the salt dried under the air-pump, and the atomic weight 2531 found; the above formula requires 2569·38. The solution of gentianine yields no precipitate with barytic salts unless it is one of gentianine; but on the addition of ammonia it becomes yellow, and yellow flakes are subsequently obtained, which resemble the above.

Gentianine and Oxide of Lead.—The neutral acetate of lead yields no precipitate in a solution of gentianine; the basic acetate or the neutral acetate and ammonia give an orange flocculent precipitate, resembling the barytic salt, and which differs as to the amount of lead according to the mode of preparation; $2PbO + C^{14} H^5 O^5$ falls from the alcoholic solution of gentianine, when it is mixed with some ammonia, and then with basic acetate of lead, taking care that the liquid still contain gentianine in solution, which is evident from its yellow colour. The atomic weight found for the salt dried at 212° was 4396, and it yielded—

Carbon	23·60	14	= 1050·0	23·86
Hydrogen	1·27	5	62·5	1·42
Oxygen	11·58	5	500·0	11·36
Oxide of lead	63·45	2	2789·0	63·36

A compound of 6 atoms of gentianine with 11 atoms of oxide of lead is obtained when an aqueous solution of the bibasic salt is mixed with an alcoholic solution of gentianine without precipitating the whole of the gentianine. The compound obtained, dried at 212°, gave—

Carbon	25·30	84	= 6300·0	25·14
Hydrogen	1·46	30	375·0	1·49
Oxygen	12·00	30	3000·0	11·98
Oxide of lead	61·24	11	15339·5	61·39

On repeating this process, other compounds of 4 atoms of gentianine to 7 atoms of oxide of lead, and of 8 atoms of gentianine to 13 atoms of oxide of lead were obtained. All the lead compounds contain a multiple of the formula $C^{14} H^5 O^5$. The compounds of

gentianine with the other metallic oxides, which were procured by precipitating their salts with gentianine, had the characteristic colours of the oxides; from a solution of silver the metal was reduced.

Gentianine and Acids.—Several acids, for instance muriatic, acetic and sulphurous acids, &c., have no action upon gentianine, and do not even render it more soluble in water. Anhydrous sulphuric acid combines with gentianine to a green liquid, when care is taken to prevent the mixture from becoming hot, and the gentianine may again be separated unaltered from this solution by carbonate of baryta. Hydrated sulphuric acid dissolves it forming a yellow liquid, from which it is thrown down unaltered by water; it is not altered by dilute sulphuric acid even on long-continued boiling. Nitric acid of 1·43 spec. grav. dissolves it with a beautiful dark green colour; a green powder is precipitated by water from this liquid, which then remains yellow. To obtain this product pure, the water should be gradually added, and with constant agitation. The precipitate, placed immediately under the air-pump and dried, contained—

Carbon	45·60	45·72	14 =	1050·0	45·90
Hydrogen	2·54	2·53	5	62·5	2·73
Nitrogen.....	7·76	..	1	175·0	7·65
Oxygen	44·10	..	10	1000·0	43·72

According to the formula $C^{14}\,H^{5}\,NO^{10}$, we should have in nitrogentianine 1 atom of nitric acid combined with 1 atom of gentianine; but since in both analyses 0·2 per cent. less hydrogen was found than theory requires, it was possible that the body contained 1 equiv. hydrogen and oxygen in the form of water, which was not entirely removed under the air-pump; on this account 0·529 grm. of substance was dried at 212°, when it lost 0·021 in weight, which nearly corresponds to 1 atom of water; hence the composition of nitrogentianine would be $C^{14}\,\frac{H^{4}}{NO^{4}}\,O^{5} + HO$. When boiled with a solution of caustic potash, sulphuric acid precipitates from the cherry-red solution reddish-yellow flakes, which are insoluble in alcohol. Nitrogentianine absorbs 2 equivs. of dry ammoniacal gas to 1 equiv. nitrogentianine; 0·519 grm. substance increased 0·0975 in dry ammoniacal gas. Dilute nitric acid has no action upon gentianine; red fuming nitric acid dissolves gentianine to a red liquid, if on each fresh addition the heating, which may extend to catching fire, is avoided. From this solution water throws down an apparently pulverulent precipitate, which however under the microscope appears to consist of acicular crystals. Owing to the small quantity of material, the amount of nitrogen could not be determined. Its composition is probably—

	Found.		
Carbon.....	42·73	14 =	42·86
Hydrogen.....	2·36	4	2·04
Nitrogen	..	2	14·29
Oxygen.....	..	10	40·81

The author obtained a different result on employing a more con-

centrated nitric acid in the preparation of a further quantity; he found 41·46 C and 1·86 per cent. H, which very nearly corresponds to the formula $C^{14} H^3 N^2 O^{11}$. When nitric acid is allowed to act for a longer time, gaseous products only are obtained; neither oxalic acid, nor any other solid product, could be found in the residuary liquid.

When chlorine is passed for some length of time into an alcoholic solution of gentianine, yellow flakes separate, which on combustion with soda and nitre proved to contain chlorine. When gentianine is fused with potash, the mass first becomes brown, then paler; and if it is then dissolved in water and accurately saturated with sulphuric acid, alcohol extracts from the residue, obtained by evaporating the solution, a salt of potash which is not oxalate of potash, and which becomes black on burning, leaving a residue of carbonate of potash. On distillation with chromate of potash and sulphuric acid, carbonic acid was evolved, and the colourless distillate contained formic acid. In accordance with the preceding analyses, the author assigns to gentianine the formula $C^{14} H^5 O^5$.—Liebig's *Annalen*, lxii. p. 106.

ANALYTICAL CHEMISTRY.

On the Estimation of Magnesia by Phosphate of Soda and of Phosphoric Acid by Magnesia. By R. Weber.

In the estimation of magnesia by phosphate of soda, or of phosphoric acid by magnesia, several phænomena occur which have hitherto been overlooked, but which have considerable influence on the results in the analysis of phosphates. When, for instance, ignited phosphate of magnesia or the ammonio-phosphate is dissolved in acids, they cannot be again completely precipitated by ammonia. The liquid filtered from the precipitate still contains magnesia, and phosphate of soda consequently produces a precipitate. The loss which occurs amounts, according to different circumstances, from 2 to 8 per cent. When the liquid contains a considerable amount of ammoniacal salts, the precipitation is more complete and the loss less than when this is not the case.

It results from numerous experiments made on this point, that the cause of this imperfect precipitation by ammonia of the phosphate of magnesia dissolved in acids is, that the solution of the ignited phosphate of magnesia, as also that of the ammonio-phosphate, does not contain the tribasic phosphoric acid, but the bibasic or pyrophosphoric acid, which does not form so insoluble a compound with magnesia as the first.

When a pyrophosphate is treated with an acid, the pyrophosphoric acid is, it is true, converted into the tribasic compound by the assimilation of 1 atom of water; but this transformation is imperfect even when the acid has been allowed to act for a considerable length

of time. Of all the acids, concentrated sulphuric acid effects this change most completely.

In two determinations of phosphoric acid by magnesia in a solution of the pyrophosphate of soda, in the first case instead of 100 per cent. only 95·26 was obtained, and in the second 94·34 per cent. $2MgO, PO^5$; while in the estimation of phosphoric acid in a solution of the crystallized phosphate of soda, or of any tribasic phosphate, the corresponding amount of pyrophosphate of magnesia is accurately obtained.

On treating the ignited phosphate of soda with hydrochloric acid, with a view to convert it into the tribasic compound, 98·22 per cent. $2MgO, PO^5$ were obtained, with nitric acid 98·17, and with concentrated sulphuric acid 99·43.

As the same circumstances obtain in the solution of the ignited pyrophosphate of magnesia in acids, it is perfectly intelligible why it is not again entirely thrown down by ammonia, and that a further precipitate is produced by phosphate of soda in the filtered liquid.

When ammonio-phosphate of magnesia is dissolved in an acid, pyrophosphoric acid is likewise eliminated, the third atom of base, the ammonia, being seized upon by the acid employed. The solution then contains pyrophosphate of magnesia, or free phosphoric acid with 2 atoms of water. However, this pyrophosphoric acid, separated in the moist way, is more readily, although not perfectly, converted into the tribasic compound by the action of the acid used as solvent than the ignited pyrophosphoric acid. This is the reason why, when ammonio-phosphate of magnesia is dissolved in an acid, it is more completely thrown down again by ammonia than is the case under similar circumstances with the ignited pyrophosphate of magnesia.

The solution of the nitrate of silver affords a certain means for ascertaining which of the two phosphoric acids are under examination. When pyrophosphate of magnesia or ammonio-phosphate of magnesia is dissolved in nitric acid and nitrate of silver added to the solution, the yellow precipitate of phosphate of silver is obtained on carefully neutralizing the liquid with ammonia. But if the experiment is made in a different manner, it is readily seen that pyrophosphoric acid has been eliminated on dissolving the magnesia-salt in an acid, but that it has for the greater part been converted into the tribasic compound by the influence of the free acid. That portion however which has not yet experienced this change may be recognised by the characteristic white salt.

If, for this purpose, ammonio-phosphate of magnesia is dissolved in nitric acid, again precipitated by ammonia, the precipitate after long standing collected on a filter, nitrate of silver added to the filtered liquid, and the ammoniacal liquid now carefully neutralized with nitric acid, a white turbidness, which after some time subsides in very distinct white flakes, results. When ignited pyrophosphate of magnesia is used for this experiment, the separation of the white pyrophosphate of silver is better seen, as in this case a larger amount of pyrophosphoric acid has remained unaltered.

Pyrophosphoric acid has no great tendency to form compounds with 3 atoms of base; certainly the third atom of base is held by a very loose affinity. Only in the single case when phosphoric acid or a phosphate is fused with an excess of carbonate of soda does it retain the third atom of base, which cannot be separated in any manner; while a solution of pyrophosphate of soda may be left for a very long time in contact with water or boiled with it; nay, even boiled with a solution of carbonate of soda, and evaporated to dryness with it, without the tribasic compound being produced. When therefore the phosphoric acid in a phosphate is to be separated and determined by magnesia, and is not contained in the solution as the tribasic compound, the phosphate must be fused with an excess of carbonate of soda. This can be done in all cases when the phosphoric acid is combined with the alkalies or those metals which are completely decomposed by fusion with carbonate of soda; but it does not succeed in converting the phosphoric acid into the tribasic compound in its combinations with the alkaline earths, as these are only imperfectly decomposed. The only way to reprecipitate entirely the pyrophosphate of magnesia from its solution by ammonia, is to heat it for some time with concentrated sulphuric acid, when on solution it can be almost entirely precipitated by ammonia.

The precipitates which the tribasic and bibasic phosphoric acids produce with magnesia differ essentially from each other by their external properties. The first is granular, crystalline, and soon subsides, especially when warmed; the latter is voluminous and flocculent, and remains long suspended in the liquid. Small quantities of pyrophosphoric acid cannot be detected or separated by magnesia.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new and œconomical Process for manufacturing the Bichromate of Potash, Chromates of Lead and Bichromate of Lime. By V. A. Jacquelain.

1. Chalk and chrome ore, previously reduced to a very fine state of division, are intimately mixed in barrels revolving upon their large axis. It is especially requisite that the ore should be finely pulverized and passed through a very fine sieve.

2. The mixture is now calcined for nine or ten hours at a bright red heat upon the sole of a reverberatory furnace, taking care to spread it equally in a layer from 5 to 6 centim. in thickness, and to renew the surface ten or twelve times with the rake. At the end of this time, if the flame was sufficiently oxidizing, the conversion of the oxide of chromium into chromate of lime is effected. This is easily ascertained; in the first place from the appearance of the sub-

stance, which exhibits a yellowish-green colour*, and then because it has the property of dissolving entirely in hydrochloric acid with the exception of particles of sand.

3. The very friable and porous mass is now crushed under a mill, mixed with hot water, and the liquid mass constantly kept in agitation, and sulphuric acid added until the liquid slightly reddens blue litmus-paper. This character indicates the complete change of the chromate of lime into bichromate, and the formation of a little sesquisulphate of iron.

4. Some triturated chalk is now gradually added to the liquor until the whole of the peroxide of iron is removed. The bichromate of lime does not by this treatment experience any change as regards its state of saturation.

5. After being allowed to stand quiet for a short time, the clear supernatant liquid, which contains only bichromate of lime and a little sulphate, is drawn off; it may now be used immediately to prepare the bichromate of potash, the neutral and basic chromates of lead, and even the chromates of zinc, which will probably ere long be consumed to a great extent in the arts, since the oxide of zinc has already taken the place of carbonate of lead in white paint with drying oil.

From the above it is seen that it is useless to prepare the bichromate of potash in order to obtain the insoluble chromates of lead, zinc, baryta, &c., which must render the preparation of these products considerably less expensive; they may readily be obtained by decomposing the bichromate of lime by the acetate or subacetate of lead, chloride of zinc, &c. With respect to the bichromate of potash, it may be as readily obtained, and in a perfectly pure state, by decomposing the bichromate of lime with a solution of carbonate of potash, which will give rise to insoluble carbonate of lime, which is easily washed, and a solution of bichromate of potash, which is concentrated and set aside to crystallize.—*Comptes Rendus*, Oct. 11, 1847.

PATENT.

Patent granted to John Robert Johnson, Nelson-square, Surrey, *for Improvements in purifying Gas, and in the Treatment of Products of Gas-Works.*

This invention consists, first, in a new mode of purifying gas (used for the purpose of illumination) from those impurities which consist of ammonia and its compounds. Ammonia exists in gas after it has passed the condensers and before entering the lime purifier, in combination with several volatile acids, for example, the hydro-

* This singular peculiarity of the chromate of lime with an excess of base, of retaining the green tint of the oxide of chromium, must have led to the belief that no chromate of lime was produced, especially as the latter is scarcely soluble in water.

sulphuric, hydrocyanic or prussic, and carbonic acid. When the gas has passed the lime purifier, these compounds have become decomposed, the lime combining with the acids before mentioned, and liberating the ammonia, which is then found in the gas in the uncombined or so-called caustic state. Various plans have been proposed to effect the separation of the ammoniacal compounds. Dilute acids have been employed, and likewise solutions of metallic salts, such as the chloride of manganese. These plans have however the disadvantage of requiring a considerable increase of pressure to force the gas through the fluid; and the use of motive power is sometimes required to render the operation successful. To obviate these inconveniences, and to effect the separation of the ammonia, the patentee employs substances possessing the property of absorbing ammonia or its compounds in the dry, or more properly speaking solid state, instead of in the state of solution, as has been hitherto practised. All the fluid substances which possess the property of absorbing ammonia and its compounds have, as far as the patentee's experiments extended, been found to possess the same property when employed in the solid state, provided they were used in a divided or pulverulent form, and that they contain sufficient water of crystallization or hygrometric moisture to bring the gas and solid matter within the sphere of affinity. The substances which possess this property may be divided into two classes:—First, those which act on the compounds of ammonia in the manner of the acids; that is to say, which absorb the ammonia only, and which liberate, or only partially absorb, the acids with which it was previously in combination. Among this class of substances are comprised the solid acids, such as the phosphoric, boracic, and other acids; the salts with excess of acid, as the bisulphates of potash, of soda and of ammonia; the biphosphates of these bases, and other salts of this class; the salts of alumina and of some other earths. Second, those substances which absorb the compounds of ammonia entirely, acid as well as base, entering into combination with the components of the substance used; the metallic salts, containing the requisite quantity of water, are comprised in this class, and will serve more or less perfectly for the purpose required; but the salts of iron and manganese, from their cheapness, will be found preferable to others.

The mode which the patentee adopts for carrying out this part of his invention is as follows:—He takes, for example, one of the substances included in the second class, viz. the sulphate of iron or common green copperas of commerce (as usually found in commerce it is in the state of crystals, dry to the touch, but containing a large quantity of combined water, or water of crystallization), and this salt he reduces to powder in the ordinary way. The finer the powder the more complete will be the decomposition of the salt by the ammoniacal compounds. This powder is employed in precisely the same manner as the moistened lime is used in what are called dry lime purifiers; that is to say, it is spread upon the shelves of a purifier, constructed like that used for the dry lime only; and the subsequent part of the process is the same as with dry lime, the cover

being lowered and sealed and the gas allowed to pass until the application of a piece of turmeric or other test-paper shows that the material ceases to absorb the ammonia. When this point is arrived at, the gas is turned into another purifier similarly prepared, and the one just saturated is emptied. It should be remarked, that although but one purifying vessel is mentioned as being used at a time, yet the operation is more perfectly effected when a series is employed, as in the lime purifiers, and is as well understood. The purifier, or series of purifiers, containing the substance used for absorbing the ammonia, is preferred to be placed so as to receive the gas before it enters the lime purifiers, as the acids in combination with the ammonia are then absorbed by the substance (when belonging to class second), the quantity of time required for the purification of the gas is diminished, and the union of one of these acids (the hydrocyanic) with the salt of iron gives rise to a useful product. When employed subsequently to the passage through the lime purifiers, one of the substances of class one will be found most advantageous.

The patentee finds the water of crystallization in sulphate of iron is sufficient to bring the salt into a fit state to effect the absorption of the ammoniacal compounds; but he does not confine himself to the use of salts in their natural state; for the salts may have a certain quantity, more or less, according to their nature, of water added beyond that which they naturally contain; the powdered sulphate of iron, for instance, if slightly moistened so that it hangs together, acts equally, as in the former case, and rests better upon the shelves of the purifier.

The second part of the invention consists in a new mode of treating the ammoniacal liquor of the gas-works, for the purpose of preparing the salts of ammonia in a purer state than they have been usually obtained, and without the noxious exhalations which attend the ordinary mode of operating. In treating the ammoniacal liquors by the ordinary process, a large quantity of highly offensive and deleterious gas (sulphuret of hydrogen) is evolved; and, to remedy this inconvenience, it has been proposed to distil the liquor, mixed with a large quantity of lime, condensing the vapours and passing the products of condensation into an acid. Another plan is, to evaporate the liquor with or without lime, and to pass the vapours through acid without condensation. In the former case, in carrying the operation into practice on a large scale, it was found that deposits of lime were obtained, and that the process was thereby rendered dangerous and otherwise objectionable. According to the second plan, unless lime be used in the evaporation, the operation is unsuccessful, as the noxious gas is generated when the vapours come into contact with the acid, and must be got rid of, thus resembling the old process. These inconveniences the patentee proposes to obviate by operating in the following manner:—The liquor is placed in a vessel similar to an ordinary steam-boiler, and heat is applied thereto by means of a furnace. The liquor consists principally of hydrosulphuret and carbonate of ammonia, with small quantities of other salts of that base. As soon as the temperature rises the hy-

drosulphuret of ammonia comes over, it being the most volatile product; a slow fire is kept up, so as to volatilize this product exclusively; and as it is given off it is conducted by a branch from a horizontal pipe into a vessel containing a solution of some substance which has the property of absorbing the sulphuretted hydrogen—the deleterious gas. The salts of iron and manganese possess this property, as has been already stated; and alkalies or lime, mixed with water, will also effect the same object. In the former case the product, after sufficient of the vapours have passed to saturate the material employed, is a solution of a salt of ammonia, holding in suspension the sulphuret of iron or manganese. In this plan, one vessel for holding the material through which the vapours are passed is sufficient; but if more be employed they are charged with the same solution. When lime or alkali is used to absorb the sulphuretted hydrogen, the ammonia is liberated, and must be conducted into a second vessel charged with an acid. At the end of this part of the operation, that is when all the hydrosulphuret of ammonia has passed over, the products found in the first vessel are sulphuret of lime and some free ammonia, and in the second a solution of a salt of ammonia. If the acid was but slightly diluted, the solution may be obtained saturated and fit to crystallize on cooling. The liquid remaining in the boiler, and now consisting principally of carbonate of ammonia, may be treated in the ordinary way for preparing the salts; that is, it may be neutralized with an acid, and the resulting solution evaporated in lead vessels, to obtain the crystals of the ammoniacal salts, as is well understood; or the evaporation may be continued in the boiler at a higher temperature, in order to drive over the other volatile salts, and the vapours passed through acid to absorb the ammonia. In the latter case the apparatus just described may be used, a cock in the horizontal pipe being opened. The vapours then pass through the horizontal pipe, and down a branch-pipe into the second vessel containing the acid, without entering the first vessel containing the lime, and are then absorbed. The evaporation is continued until the volatile salts of ammonia are all driven off, when the liquor in the boiler may be rejected, unless it be found that the fixed salts remaining in the liquor are in sufficient quantity to be worth extracting, which may be ascertained approximatively by evaporating a drop of the liquor on a strip of glass, or accurately by evaporating nearly to dryness a known quantity of the liquor, and by weighing the resulting salt. These fixed salts may be obtained by entirely evaporating the liquor in a leaden vessel, or by adding to the liquor while in the boiler a certain quantity, more or less, according to the amount of the fixed salts present, of sulphuret of lime in solution. This substance may be obtained from the first part of the operation when lime is used, or from the liquor of the wet purifiers of the gas-works. The sulphuret of lime decomposes the fixed salts of ammonia, liberating the latter substance in the state of hydrosulphuret, which may be treated in the same manner as that evolved in the first stage of the process.—Sealed Dec. 20, 1845.

THE CHEMICAL GAZETTE.

No. CXXIII.—December 1, 1847.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Action of Hydracids upon Oxyacids. By C. Lecomte.

The action of hydracids upon the oxyacids has not hitherto been investigated in a general manner. We possess, in fact, but a memoir by M. Baudrimont upon the formation of nitromuriatic acid, by the reciprocal action of hydrochloric and nitric acids dissolved in water; and a notice by M. Millon, who observed that sulphuretted hydrogen was without action upon nitric acid previously deprived of hyponitric acid by means of nitrate of urea and diluted with twice its volume of water. I trust therefore that the following researches will prove interesting to chemists.

The apparatus which I have employed to study the action of hydrosulphuric acid upon nitric acid is very simple. It is composed of a balloon communicating with a washing-flask, and this with a second flask surmounted by a tube for collecting the gases; when all is thus arranged, some fragments of the sulphuret of antimony and hydrochloric acid are conveyed into the balloon and some milk of lime into the washing-flask. The balloon is placed over a charcoal furnace. When all the air of the apparatus had been expelled, 85 grms. of nitric acid of 1·33 spec. grav., freed from hyponitric acid by means of nitrate of urea, were poured into the second flask kept in water, which was carefully maintained at a temperature of 64°–68° F.

On the appearance of the first bubbles of sulphuretted hydrogen in the nitric acid, a considerable number of minute bubbles were observed to be disengaged from different points of the liquid; at the same time sulphur separated and remained in suspension; the atmosphere of the flask became of an orange colour, and the nitric acid so intensely green as to prevent the passage of light; gradually this colour diminished, and the sulphur aggregated into a mass at the surface of the liquid. The action was continued until the sulphuretted hydrogen passed through the nitric acid without experiencing any change.

The sulphur obtained in this manner formed an opake spongy mass of a pure yellow colour. After freeing it by washing from the acid liquid it contained, although obtained in the cold, it exhibited all the elastic properties presented by soft sulphur obtained with the

assistance of heat and immersion in cold water. Nevertheless, in the circumstances under which the experiments were made, the temperature never rose above 68°–77°; the chemical reaction sufficed therefore to produce a phænomenon which under ordinary circumstances requires an elevation of temperature of about 482°. This sulphur was kept for eight days in water; it was still somewhat elastic, and its colour had but slightly decreased.

The gases which are disengaged in the preceding operation vary according to the period when they are collected. At the commencement, and for about three hours, they consist of a mixture of deutoxide of nitrogen and of hyponitric acid; the latter gradually disappears, and is replaced by sulphuretted hydrogen. It will presently be seen that the presence of one of these two gases in a mixture indicates the absence of the other; in a word, these two gases are incompatible.

The mixture of deutoxide of nitrogen and of sulphuretted hydrogen, which is disengaged during the remainder of the operation, exhibits a very remarkable phænomenon; it is partly decomposed in passing through water, which is rendered milky by the eliminated sulphur; but the bubbles which burst at the surface form, when the air is undisturbed, very regular rings, analogous to those presented by phosphuretted hydrogen when it ignites spontaneously on its issue from water. This phænomenon is readily explained by the action of hyponitric acid upon sulphuretted hydrogen; these two gases being incompatible, and each bubble being a mixture of sulphuretted hydrogen and deutoxide of nitrogen, the air acting upon the latter by its oxygen converts it into hyponitric acid, which in its turn decomposes the sulphuretted hydrogen; and as this action is only exerted upon the central and peripheral parts which are in contact with the air, the rings above mentioned are formed.

The following experiments prove decidedly that hyponitric and hyposulphuric acids are not compatible. If a bell-glass containing a mixture of deutoxide of nitrogen and sulphuretted hydrogen is observed, the gases are not decomposed immediately; but on introducing merely a few bubbles of oxygen, the gases are coloured, sulphur is deposited upon the sides of the vessel, and the colour disappears; a further addition of oxygen reproduces the same phænomena, which can be repeated until the sulphuretted hydrogen has entirely disappeared. This curious reaction of the deutoxide of nitrogen promises to be of considerable importance in the industrial arts. Sulphur does not occur in France, but considerable quantities of sulphate of lime; this decomposed with coal, and the moist sulphuret obtained decomposed in its turn by the carbonic acid derived from any furnace, would yield sulphuretted hydrogen. This gas, conveyed into a chamber containing air and deutoxide of nitrogen, would furnish water and sulphur; so that a small quantity of deutoxide of nitrogen would suffice in this case, as in the preparation of sulphuric acid, for the transformation of a large quantity of the reacting bodies.

In Berzelius's 'Manual of Chemistry,' it is stated that the deut-

oxide of nitrogen and sulphuretted hydrogen are mutually decomposed; that sulphuret of ammonium or the hydrosulphate of ammonia and the protoxide of nitrogen are formed. This reaction is true when the gases are moist, but when dry they do not react upon each other.

The liquid derived from the action of the sulphuretted hydrogen upon the nitric acid was separated from sulphur and again mixed with the wash-waters of this latter body; the whole was saturated hot with carbonate of baryta until the appearance of a slight ammoniacal odour; a few drops of sulphuric acid were added to neutralize the liquid; it was then thrown upon a filter, the precipitate of sulphate of baryta well washed, and all the liquids united and evaporated until there remained but 100 grms.; the crystalline residue kept for several hours at a temperature of 113°, weighed 3·80 grms. Analysis has proved that this salt is formed almost entirely of sulphate of ammonia, containing so minute a quantity of the nitrate that the protosulphate of iron is scarcely coloured by it in the presence of sulphuric acid.—*Ann. de Chim. et de Phys.*, Oct. 1847.

On some Properties of Palladium. *By* N. W. Fischer.

The following observations are intended to correct several statements which have been admitted into chemical works respecting this metal, particularly in reference to its behaviour towards acids and alkalies. At the ordinary temperature palladium dissolves slowly and without any evolution of gas in *nitric acid*; the liquid which thus becomes charged with nitrous acid gradually ceases in closed vessels to oxidize the metal, but with access of air it still acts, although slowly. When palladium is heated with nitric acid, nitric oxide is disengaged as with other metals, and it is quickly dissolved. When the solution, obtained either at the ordinary temperature or with the assistance of heat, is dried over caustic lime in the exsiccator, the protonitrate of palladium is obtained in minute rhombic prisms of a brownish-yellow colour or as a brownish-red mass; in both cases it deliquesces in the air, and dissolves in water with a brown colour; very dilute solutions are yellow. The concentrated solution of this salt, and the dilute still more rapidly, gradually deposit the whole of the salt as a basic protonitrate of palladium, so that mere traces can be detected in the liquid. When the solution of the protonitrate of palladium is evaporated, nitric acid escapes with the water at 77°–86°; and on dissolving the salt dried at this temperature in water, a residue of basic insoluble salt is left. If the salt is evaporated between 212° and 248°, nearly the whole is converted into basic salt, and becomes insoluble; and between 248° and 266° nearly the whole is changed into protoxide. The basic salt dried between 212° and 248° absorbs no moisture from the atmosphere.

The welded metal does not dissolve in *sulphuric acid*; in the porous state, as it is obtained by igniting some of its salts, and likewise in the state of filings, it dissolves in this acid with a reddish-brown colour, with disengagement of sulphurous acid. The very

acid reddish-brown solution is not rendered turbid by dilution with water, and the salt is readily soluble in water. Both solutions are of a yellow colour; however, this is not an advantageous method of preparing the protosulphate of palladium, as the excess of sulphuric acid cannot be removed from the salt, which is decomposed at the temperature of its boiling-point; and the method adopted by Kane, of employing nitric and sulphuric acid, is preferable.

Muriatic acid, which acts but slightly upon the welded metal, entirely dissolves porous palladium and filings at a gentle heat; but to obtain a solution of the metal in muriatic acid, the best plan is to pass chlorine into the liquid until the metal is wholly dissolved. If an addition of nitric acid is used instead of the chlorine, the salt evaporated at 212° is not pure protochloride, but contains some nitrate; for the protochloride crystallized from solutions containing no nitric acid remains dry in the air, while that containing nitrate is thereby rendered deliquescent. At higher temperatures this salt behaves like the nitrate; it first passes into basic salt, and then into subchloride. The aqueous solution of the protochloride likewise deposits a basic salt after some time. The other acids do not act on metallic palladium, except phosphoric, which when fused with the powdered metal disengages some phosphorous acid, but does not dissolve any oxide, because this is again immediately converted into metal by the temperature required.

Potash and *soda* precipitate from neutral solutions of the protonitrate of palladium a basic salt, which is insoluble in an excess of the precipitant, and is converted on boiling with it into hydrated protoxide. Carbonate of potash and soda produce, neither in acid nor in neutral solutions of the protoxide, any precipitate, and no carbonic acid is disengaged on their addition to neutral solutions; the liquid merely assumes a darker colour. On boiling this liquid, basic protocarbonate of palladium subsides; the supernatant liquid has a light brown colour, but contains mere traces of the protoxide in solution. The above alkalies behave in the same manner towards solutions of palladium in sulphuric and muriatic acids; but the caustic alkalies redissolve the precipitate thrown down from the last acid. *Ammonia* and *carbonate of ammonia* act in a totally different manner; they precipitate only a portion from the solution of the protonitrate as basic salt; the remainder forms a double salt with the nitrate of ammonia, which is obtained in colourless prisms on evaporating the solution. If a solution of this double salt has been decanted from the precipitated basic salt, the latter does not dissolve on boiling with ammonia, but is left in the state of protoxide, containing ammonia. Solutions of the metal in sulphuric acid behave in the same manner, only that none or very little basic salt is deposited on the first addition of ammonia, and this dissolves readily on a further addition. Ammonia produces in the solution of the protochloride at first a brown precipitate of the basic salt, which is converted on a larger addition into a peach-red double salt; and a still greater excess dissolves this precipitate to a colourless liquid, from which white prisms crystallize on evaporation. This complete solu-

tion in ammonia occurs however only when the chloride has been prepared without the use of nitric acid; if it contain any protonitrate, a corresponding quantity of a brown residue is left.

As is well known, ammonia forms with the salts of palladium and the above-mentioned acids mostly two, and with the protochloride three double salts. The first of these double salts contains 1 atom of protosalt of palladium to 2 of ammonia, and has already been described under the several acids as colourless. The second double salt is obtained by depriving the preceding salts of a portion of their ammonia, either by the addition of acids or the application of heat. The salts thus produced are yellow, and contain 1 atom of protosalt of palladium to 1 of ammonia. The double salts of ammonia with the protochloride have the same constitution as the preceding; the colourless salt contains 1 atom of protosalt of palladium to 2 of ammonia; the other two are isomeric; one is red, the other yellow, and both contain 1 atom of ammonia to 1 of chlorine. The yellow salt dissolves when pure entirely in water, while the red, as observed by Fehling, is decomposed on boiling with water. The red salt, when dissolved in ammonia, is precipitated by muriatic acid from this solution as yellow salt, while ammonia throws down the red salt from a solution of the yellow one in muriatic acid. The author does not confirm the conversion of the red into the yellow salt by heating it when moist up to 212°.

The double salt formed by the protochloride and chloride of potassium is in minute slender prisms of a beautiful bronze colour; the larger crystals are brown by reflected and green by transmitted light. Besides these salts there are other combinations of the perchloride with the chlorides of the alkalies, which have a vermilion colour. It is easy to obtain them by adding chloride of potassium to the hot solution of the protochloride of palladium and potassium in *aqua regia*. A prismatic crystallized yellow double salt of protonitrite of palladium and nitrite of potash, and a similar fibrous one of soda, are obtained when nitrite of potash or soda is added to the solution of the pure protochloride until the brown colour of the liquid is changed into a greenish one, when the liquid is evaporated. Ammonia forms two salts with nitrite of palladium with 1 and 2 atoms of ammonia, of which the latter is colourless and the first yellow, as with the other ammoniacal salts of palladium.

The results respecting those salts of palladium which are obtained as precipitates agree less than the preceding experiments with those obtained by Kane; thus, for instance, the author found it impossible to obtain a yellow precipitate from a solution of the protochloride either by mixing with phosphates or tartrates. Neutral tartrate of potash produced no precipitate in solutions of palladium in whatever proportion it was added, and phosphate of soda threw down a mucilaginous precipitate of basic protochloride, which contained no phosphoric acid. Oxalate of potash precipitated a salt from the protochloride in very minute needles, but which is not oxalate of palladium as stated, but a double salt with oxalate of potash. Neither the neutral nor the binoxalate of ammonia formed any precipitate

in the solution. Tannic and formic acids throw down metallic palladium from its solutions. The above-mentioned combination of the protoxide of palladium with ammonia, which is formed when the protonitrate is acted upon with an excess of ammonia and the precipitate boiled with ammonia, is when dry of a grayish-black colour. At a gentle heat it detonates faintly, liberating water and nitrogen, while the metal is left in the form of a granulated powder. Its composition is $PdO + NH^3$.

Highly characteristic of palladium is the reaction with protochloride of tin, with which it forms a brown precipitate, which dissolves in muriatic acid with a green colour. Protochloride of tin consequently produces this green colour immediately in muriatic solutions of palladium; and even when but a millionth of palladium is contained in the solution, this colour is still distinct; so that palladium may be as readily detected by this means as by the reaction with iodide of potassium.—Poggendorff's *Annalen*, lxxi. p. 431.

Further Researches on the Dehydration of Ammoniacal Salts and Amides. *By* Messrs. Dumas, Malaguti *and* Leblanc.

In continuing our researches on this subject, we have met with some new facts, which leave nothing to be wished for, as regards the production and nature of the substance derived from the acetate of ammonia. The body $C^4 H^9 N$ is not only isomeric with the hydrocyanate of methylene, but all its properties and its reactions establish their absolute identity.

The hydrocyanate of methylene, analogous to the hydrocyanic æther of M. Pelouze, had not hitherto been obtained and investigated. We have prepared it easily by acting with dry cyanide of potassium upon the pure sulphate of methylene. As soon as we had succeeded in overcoming some difficulties of purification, the two products of such different origin proved to be perfectly identical in every respect. In the reaction yielding the hydrocyanate of methylene by means of cyanide of potassium, a product contaminated with hydrocyanate and formiate of ammonia imparts to it an insupportable odour and taste, as well as most poisonous properties; by boiling this product, at first with some binoxide of mercury, and then over anhydrous phosphoric acid, it is obtained with all the properties and even the odour of the product procured from the acetate of ammonia*.

This product, which we shall henceforth call the hydrocyanate of methylene, whatever its origin, is not decomposed by the hydrated alkalies, like the compound æthers; no cyanide is produced, no alcohol regenerated; there is simply a fixation of water and formation of alkaline acetate, with disengagement of ammonia. The hydrocyanic æther of M. Pelouze behaves in an analogous manner when treated by alkalies, no alcohol being formed.

Since our last communication we have had occasion to examine the action of anhydrous phosphoric acid upon some amides, and the

* The pure hydrocyanate of methylene is far less poisonous.

results we have found confirm the assertion then made. Butyramide and benzamide yielded with the greatest facility the same products as their ammoniacal salts. Valeriamide would undoubtedly yield the same product as that which we obtained from the valerianate of ammonia, and which appears to be identical with the valeronitrile discovered by M. Schlieper on treating gelatine with chromic acid.—*Comptes Rendus*, Oct. 4, 1847.

Observations on Cyanogen and Paracyanogen.
By Dr. Delbrueck.

We are acquainted with several modes of formation of cyanogen, the latter being produced whenever one of its constituents comes into contact in the moment of elimination with the other under suitable circumstances and in the presence of an alkali. Thus cyanogen is produced when ammonia is passed over incandescent coals, and when carbonate of potash is heated to redness with charcoal containing nitrogen. Even Scheele prepared cyanogen by heating charcoal-powder or graphite to redness with bitartrate of potash and some chloride of ammonium. But most worthy of attention is the production of cyanogen, described by Desfosses and Fownes, on heating to redness pure vegetable charcoal or charred sugar with carbonate of potash, which however has hitherto remained somewhat doubtful. The following experiments show that under certain conditions cyanogen may be formed from entirely inorganic elements; and that wherever carbon or nitrogen is set free from a compound in the presence of the other and of an alkali, cyanogen is constantly produced. On heating to redness a mixture of charred sugar or graphite with carbonate of potash and nitrate of ammonia, cyanogen is formed in abundance. Further, on heating to redness the compound obtained by igniting potassium in carbonic oxide, cyanide of potassium is formed; the same result is obtained on passing ammonia and carbonic acid at the same time over ignited potassium, or on melting potassium with some pieces of carbonate of ammonia. Finally, cyanide of potassium is formed on passing a mixture of pure nitrogen and carbonic acid over ignited potassium. In the experiments hitherto described, one of the elements has constantly come in contact with the second in a nascent state. On a repetition of the above experiment of Desfosses and Fownes this was likewise confirmed; cyanogen could be distinctly detected in the residue, although its amount was small. This experiment proves that cyanogen may also be formed by the direct union of the carbon and nitrogen whenever an alkali is present, and that consequently cyanogen may be produced from entirely inorganic elements.

Paracyanogen, the brown residue which remains on heating the percyanide of mercury, was first examined by Prof. Johnston, who found it to possess the same composition as cyanogen. Cyanide of silver allows half its cyanogen to escape, while the other half is left behind in the solid state. Among the other methods of preparing paracyanogen is passing cyanogen gas into water, and allowing it to

stand for a long time; or passing this gas into a concentrated solution of caustic potash, when paracyanogen is immediately formed. The author obtained a considerable quantity of paracyanogen by digesting cyanide of potassium with sulphuric acid, when it is produced by the reaction of the free prussic acid upon the cyanide of potassium; it is also obtained by passing prussic acid into a solution of cyanide of potassium. The metamorphosis of concentrated prussic acid into paracyanogen is well known; according to the author a dilute solution may likewise be converted into paracyanogen by the addition of some cyanide of potassium. The several substances, however, comprised under the name of paracyanogen, have different properties and a different composition. Paracyanogen is only obtained pure from cyanide of mercury, if the latter was absolutely dry before being heated; from moist cyanide products are obtained which have assimilated the elements of water, and have thus partially lost their insolubility in water. Thaulow has stated that the hard, brittle, silver-gray substance which remains on heating cyanide of silver is paracyanide of silver. The author considers it improbable that the cyanogen which escapes in this reaction, and which Thaulow has called carbazotic gas, because it possessed according to him different properties from cyanogen, is a distinct modification of cyanogen, as he was unable to verify the differences enumerated by Thaulow; he also doubts the residue being paracyanide of silver, and is rather inclined to regard it as a mixture of silver with paracyanogen; for nitric acid instantly removes a portion of the silver, but then leaves a brown residue, which still contains a considerable quantity of silver which cannot be extracted by the acid. Whether this residue is paracyanide of silver cannot be positively asserted. Liebig entertains a different view respecting this residue; he regards it as a mixture of 1 atom of mellonide of silver with 2 atoms of carbon, because after having exhausted it twice with boiling nitric acid, he found it to contain 48·3 per cent. silver, which corresponds to 3 atoms of cyanogen to 1 of silver, or what is the same thing, to 1 atom of mellonide of silver and 2 atoms of carbon. The author considers the above quantity of silver to be accidental, since by repeated boiling with nitric acid further quantities of silver could be removed; moreover Liebig found the mixtures of nitrogen and cyanogen formed on heating cyanide of silver to be in the different tubes in the proportion of 1 : 8; 1 : 5; 1 : 4; 1 : 8, while mellon should have yielded the proportion 1 : 3. The author exposed Thaulow's paracyanide of silver in an exhausted flask to an intense red heat, and examined the gases evolved; he found the relation of nitrogen to cyanogen in four different tubes to be 1 : 1·5; 1 : 2·4; 1 : 0·86; 1 : 0·9; these quantities correspond to no simple proportion, and the amount of nitrogen decreases towards the end of the operation. Moreover, the author could find not the least trace of mellon in the residue left on heating cyanide of silver to redness.

The paracyanogen which is formed by the action of chlorine upon cyanide of potassium is not a pure product, and behaves very differently from the preceding. It dissolves partially in water, and the

residue for the greater portion in nitric acid. The paracyanogen prepared by igniting moist percyanide of mercury is likewise partially soluble in water. That produced by the reaction of prussic acid upon cyanide of potassium could not be obtained of constant composition; like the latter it dissolves partially in water and acids. Apparently that obtained from dry cyanide of mercury and cyanide of silver is alone of constant composition.

The pure paracyanogen obtained from cyanide of silver or cyanide of mercury is in no way altered by nitric acid; all the other paracyanogen compounds are partially dissolved by it, and again separated from these solutions by water. Lead- and silver-salts precipitate the substances in solution more completely. When the solution of paracyanogen prepared by acting upon cyanide of potassium with hydrocyanic acid is thrown down with nitrate of silver, and the precipitate filtered, ammonia produces in the clear liquid an abundant precipitate, which still contains silver. Ammonia alone precipitates the compound contained in the solution in the form of a thick brown precipitate. When a small quantity of ammonia is added to the solution not sufficient to produce any precipitation, the addition of acetate of lead immediately causes a thick white precipitate; salts of copper yield a light green, and salts of manganese, after the addition of chloride of ammonium, a light brown precipitate. The substance contained in the solution is a mixture of different compounds; the salt precipitated by nitrate of silver without ammonia contained 31·976 per cent. oxide of silver; that from the filtered solution by ammonia only 3·069 per cent. oxide of silver. The salt precipitated by nitrate of silver and ammonia contained 19·347 per cent. oxide of silver.

Paracyanogen procured from dry cyanide of mercury experiences considerable changes by heat. When gradually raised to a high temperature, the paracyanogen is decreased to about one-eleventh of the amount first eliminated; it formed a light voluminous mass, which at a strong red heat in a current of carbonic acid was entirely volatilized, being converted into cyanogen. The result was the same when paracyanogen prepared in a different manner was treated in the same way, except that a slight residue of charcoal remained in the experiments made with it, which in the case of the paracyanogen procured from moist cyanide of mercury burnt to carbonic oxide. The result was likewise the same when nitrogen was used instead of carbonic acid. It is seen that each of these paracyanogens can be again transformed into cyanogen when heated to redness in an indifferent gas. In a current of hydrogen the elements of each kind of paracyanogen combine at a low temperature to form prussic acid and ammonia, leaving a residue of carbon, which is most considerable in the impure kinds,

$$2C^2N + 4H = C^2NH + NH^3 + 2C.$$

Since it appeared not improbable that the animal and vegetable charcoal contained the nitrogen, which cannot be expelled by continued ignition, in the form of paracyanogen, both were heated at

first alone, and then in hydrogen; but in both cases only traces of cyanogen were given off.

The action of chlorine upon paracyanogen is very remarkable; with pure heated paracyanogen white vapours were produced, which possessed a suffocating odour, and condensed to a solid in the cold parts of the apparatus. This solid mass was not altered by exposure to the air, dissolved in hot water, but did not react as cyanogen. After fusion with carbonate of soda, however, this reaction took place, and salts of silver likewise indicated the presence of chlorine. On account of the small quantity obtained, this body could not be more minutely examined. The same body was likewise produced from paracyanogen from cyanide of potassium and prussic acid, but together with solid chloride of cyanogen, which was evident from the well-known mouse-like odour; and probably also with gaseous chloride of cyanogen, as the gas disengaged from the apparatus possessed a suffocating odour.

Chlorine combines with each of the above-described modifications of paracyanogen, forming solid chloride of cyanogen along with other products, which require further investigation. From what has been stated, it is seen that all the kinds of paracyanogen are reconverted, when heated to redness in an indifferent gas, into cyanogen, with or without a residue of carbon; that they all form prussic acid and ammonia when ignited in hydrogen, and chloride of cyanogen in chlorine. They all therefore certainly contain the pure compound, more or less contaminated with products of decomposition.—*Journ. für Prakt. Chem.*, xli. p. 162.

On the Bile of the Pig. By MM. STRECKER *and* GUNDELACH.

The authors consider that their researches on the bile of the pig afford a further support to the theory on the constitution of the bile, according to which it must be regarded as a kind of soap. In fact, pigs' bile is a mixture of potash, soda and ammonia salts of an acid which is nearly related in certain respects to the fatty acids.

The *hyocholeic acid* differs from the acid of ox-bile (the choleic acid of Demarçay) in not being soluble in water, yielding insoluble precipitates with lime, baryta, &c., and in containing no sulphur. Its formula is $C^{54}\,H^{43}\,NO^{10}$, and it combines with bases without any elimination of water. It is evident that hyocholeic acid cannot yield any taurine, and the authors have assured themselves that this substance is not contained in the fresh bile. The bile precipitated by acetic acid, and the liquid separated from the precipitate and evaporated to dryness, leaves a residue which contains only chloride of sodium and sulphates.

When the bile of the pig comes into contact in the animal œconomy with chyme, which has always an acid reaction, hyocholeic acid must necessarily be precipitated, and the acid reaction of the chyme neutralized. It would undoubtedly be highly interesting to investigate the process of digestion in the pig. In the Ruminants it is observed that the acid chyme mixed with the bile slowly loses its

acidity, although ox-bile for instance is not precipitated by acids diluted with water. The opinion that the difference in composition of the bile is connected with the digestive system, which is highly complicated in the ruminants, is perhaps not altogether devoid of foundation.—*Comptes Rendus*, July 19, 1847.

On the Action of Zinc upon Selenious Acid. By Prof. Wöhler.

Zinc does not behave towards selenious acid exactly in the same manner as to sulphurous acid; there is no acid of selenium corresponding to the dithionous acid formed; but selenium is reduced, and an acid selenite of zinc obtained, which had not hitherto been noticed. When a bright piece of zinc is placed in a moderately-concentrated solution of selenious acid in water, it soon becomes coated with a thin layer of reduced selenium, while a thick liquid is seen to flow from its surface. No decomposition of water occurs. To expedite the action, it is best to take a large excess of bright zinc-filings. They are gradually converted into a mixture of seleniuret of zinc and free selenium. The filtered liquid can be evaporated at a very gentle heat to a certain degree; but as soon as it becomes more concentrated, this is no longer possible without decomposition taking place; it is consequently allowed to evaporate spontaneously or *in vacuo* over sulphuric acid. Only when it has become syrupy, and after standing for several weeks, large yellow crystals of the acid salt are formed in it, which are dried between folds of fine filtering-paper. On analysis the salt gave—

	Found.	Theory.
Oxide of zinc	14·86	13·97
Selenious acid	76·03	76·72
Water	9·10	9·31

It is consequently a compound of the neutral selenite of zinc with 3 atoms of hydrated selenious acid = $ZnO, SeO^2 + 3HO, SeO^2$. It forms very large crystals of a pure yellow colour, exactly like the neutral chromate of potash; they are oblique rhomboidal columns. The salt is not altered by exposure to the air, dissolves readily in water, forming a colourless solution which has a strong acid reaction, and is not altered by acids. When however it is heated, it becomes turbid, the salt being decomposed into selenious acid and neutral selenite of zinc, which separates as a colourless crystalline powder, and only after being long in contact with the liquid dissolves again. When a crystal is heated to between 86° and 104° F., it experiences the same decomposition, becoming white and opake. At a higher temperature it melts, parts with water, and at last selenious acid sublimes; the residue consists of the neutral or basic salt according to the temperature employed.—Liebig's *Annalen*, August 1847.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of the Inorganic Constituents in Organic Bodies, and particularly on the Estimation of Phosphoric Acid. By M. Heintz.

The author has been led, in his experiments on ash analyses, to the same method of charring the organic substances which Prof. Rose has characterized as the most rational. For a long time he has employed it in his laboratory, and its numerous advantages have been very evident in these experiments. In those cases, however, in which the ash contains alkaline carbonate and phosphate, some of the carbonic acid is found to be expelled even at the low temperature used for charring, a phosphate being formed with 3 atoms of alkaline base; consequently the amount of alkali combined with carbonic acid or with an organic acid, deduced from the quantity of carbonic acid, turns out too small according to this method if care is not taken to eliminate the error. It was found impossible to exclude it by endeavouring to convert the above phosphate by means of carbonic acid into the ordinary phosphate and carbonate of soda, as it was experimentally proved that the pyrophosphate of soda which may occur in charred substances is decomposed by the action of carbonic acid into acid pyrophosphate and carbonate of soda.

Now since it must be admitted that the alkaline phosphates which occur in such organic bodies as contain organic or carbonated salts are not acid, and since, on the other hand, owing to the carbonic acid which constantly occurs in organic bodies, they cannot exist in them in combination with 3 atoms of fixed base, M. Heintz advises determining the amount of carbonic acid in the following manner:—The charred mass is digested with muriatic acid, the liquid filtered, and the residuary ash exhausted with water; the liquid is then evaporated to dryness and the residue heated to faint redness. Upon this the quantity of chlorine contained in the residuary saline mass is ascertained; the difference between this quantity and that obtained from another portion of the organic substance is the quantity of chlorine equivalent to the amount of carbonic acid expelled. The author has convinced himself that phosphate of soda, $3NaO, PO^5$ is decomposed by the muriatic acid entirely into $2NaO + HO\,PO^5$ and chloride of sodium, and that on evaporating the acid liquid and retaining the residue for some time at a faint red heat, nearly the whole excess of muriatic acid can be driven off. Nevertheless, in his experiments he constantly obtained a small excess. But since, on the one hand, the amount of alkaline phosphate which may occur in organic substances is very small, and, on the other hand, it follows from the author's experiments that the results obtained according to his method approach nearest to truth, he considers himself justified in preferring it to all that have hitherto been recommended. The pyrophosphoric acid formed on heating to redness cannot give rise to any error, as on evaporating the acid liquid it is converted into the ordinary phosphoric acid. To ascer-

tain the entire amount of fixed constituents of an organic substance, the author advises uniting the muriatic extract of the charred mass with the ash, which is subsequently left on burning, evaporating it to dryness, heating to a faint red and weighing. Now there is found just so much more by weight as the quantity of chlorine equivalent to the found quantity of carbonic acid weighs more than the sum of the quantity of carbonic acid and its equivalent amount of oxygen. Consequently a sum a 0·246 (when a represents the amount of carbonic acid found) must be subtracted from the ascertained amount of fixed constituents in order to obtain the exact quantity contained in the organic substance.

We now proceed to describe the author's method of separating phosphoric acid from the alkaline earths and alkalies. Since, according to Mitscherlich's experiments, the phosphate of lead is insoluble in acetic acid, and, contrary to the statement of Brett, barely a trace is dissolved by solutions of chloride of ammonium, he recommends precipitating the phosphoric acid from a solution of the salts in acetic acid with nitrate of lead. But as the precipitate is not pure phosphate of lead, but always contains chloride, if chlorine were present in the solution the quantity of the acid cannot be directly ascertained by weighing this precipitate. It must be decomposed with sulphuric acid and alcohol, and the phosphoric acid in the liquid filtered from the sulphate of lead precipitated with ammonia and sulphate of magnesia.

In the experiments which the author was led to make to test the accuracy of this method, he found, as above stated, that the phosphate of lead, when precipitated from a solution containing chlorine, constantly carries down with it some chlorine, which cannot be removed by washing with hot water, however long continued. This induced him to submit the composition of the phosphates of lead to fresh examination, especially as Berzelius states that the purest phosphate of lead was obtained by precipitating chloride of lead with phosphate of soda. The author prepared four different combinations of lead with the ordinary tribasic phosphoric acid.

I. $3(PO^5+3PbO)+ClPb+HO$ is formed when a boiling solution of chloride of lead is precipitated by an excess of ordinary phosphate of soda, and the white amorphous precipitate washed with boiling water. This compound dissolves readily in dilute nitric acid, and does not alter its colour when ignited before fusing, when it gives off water and sometimes traces of chloride of lead. Before the blowpipe it melts to a bead, which on cooling exhibits the usual phænomena of crystallization and incandescence. In its ignited state this combination has the same composition as the native phosphate.

II. $2(PO^5, 3PbO) + ClPb$ is formed when a boiling solution of chloride of lead is imperfectly precipitated by phosphate of soda. This compound differs from the preceding only in parting with little or no water when heated, becoming at the same time yellow, which colour however again disappears on cooling. By long-continued strong red heat this compound can be entirely converted into that which occurs native, as Buntbleierz.

III. PO^5, 2PbO + HO is obtained when a boiling solution of nitrate of lead is precipitated by pure phosphoric acid. It forms a beautiful white crystalline precipitate of considerable lustre, which may be readily washed with water. This compound does not assume a yellow colour when heated, but it parts with its water, and is converted into pyrophosphate of lead. It fuses readily to a bead, which however does not crystallize on cooling nor exhibit the phænomenon of incandescence.

IV. PO^5, 3PbO is obtained according to the methods directed by Berzelius and Mitscherlich, by digesting the preceding salt with ammonia, and by imperfectly precipitating acetate of lead with phosphate of soda. A white amorphous precipitate subsides, which perfectly resembles the two first-mentioned compounds, but it contains no chloride of lead.

When a solution of nitrate of lead is precipitated with ordinary phosphate of soda, a mixture of the two last salts subsides. If, on the other hand, a solution of chloride of lead is precipitated with biphosphate of soda, a mixture of the salts described under II. and III. is deposited.

M. Heintz then describes an easy method of separating magnesia from the alkalies, which is very useful in ash analyses. Magnesia is precipitated by phosphate of ammonia and free ammonia, the precipitate washed with water containing a little ammonia, ignited and weighed; the filtered solution is evaporated to expel as much as possible of the free ammonia; and the hot liquid, which must contain some chlorine, precipitated with nitrate or acetate of lead, a mixture of ammonia and carbonate of ammonia added and the whole filtered; the liquid now contains neither lead nor phosphoric acid sufficient to occasion any perceptible error. The alkalies can then be determined in the usual manner. This method is naturally not applicable when lithia is present.

A new Method for determining the Amount of Carbonate of Lime. *By* M. Bineau.

The object of this method of analysis is to afford an easy and expeditious means of estimating the carbonate of lime contained either in calcareous rocks, marls, arable soils, or in waters. When the substance is solid, the portion to be examined is conveyed into a tubulated retort, after having been finely powdered if necessary; weak hydrochloric acid of a fixed strength is added in known quantity, and more than sufficient to decompose the carbonate; the whole is heated until a few drops begin to condense on the neck of the retort; a tubulated receiver is then adapted, and the whole made to boil. By operating in this manner, the carbonic acid absorbed by the distilled liquid may be neglected without inconvenience. When the ebullition has lasted sufficiently for the reaction to be complete, the liquids in the receiver and the retort are united, and after having coloured the mixture with a small quantity of a neutral solution of litmus, a solution of caustic alkali of known

strength is poured into it from a graduated burette, stopping the moment the colour passes into blue.

If the limestone contains magnesia, an additional operation is requisite in order to estimate the magnesia, which would cause an error in the amount of lime from its neutralizing part of the acid. To complete the analysis, it suffices to add some sugar-water and further additions of the normal alkali as long as a precipitate results; the lime is held in solution by the sugar, and the magnesia alone is precipitated. Its amount, or that of its carbonate, is deduced from the volume of alkali consumed in the second part of the assay. If the exact amount of alkaline liquid has been exceeded, it is easily remedied by estimating the excess; the magnesia is collected on a filter, and the volume of acid of known strength requisite to destroy the alkalinity of the liquid is determined.

In all cases when magnesia has been detected and its amount ascertained, it is necessary, in order to calculate the proportion of lime, to subtract from the acid employed at the beginning of the experiment not only that corresponding to the alkali first added to neutralize, but likewise that corresponding to the alkali which displaced the magnesia. In order to obtain as accurate an estimation of the magnesia as possible, care should be taken not to operate on too much liquid, owing to its solubility. The presence of the sugar or of an alkaline salt does not increase the solubility of magnesia.

The presence of alumina and of peroxide of iron has no influence on the results of the analysis. Manganese and protoxide of iron would prevent the estimation of the magnesia, but not that of the lime; moreover, the alteration which these precipitated oxides would experience from exposure to the air would furnish a ready sign.

If the substance under analysis contain carbonate of potash or soda, these salts will have to be previously removed by washing, or their quantity determined that they may be subtracted.

It is needless to observe that nitric acid, and even sulphuric acid, may be employed in this analysis.

We will now consider the case where the carbonate of lime is dissolved in water. If the carbonate of potash or soda, or other salts with an alkaline reaction, or organic substances capable of yielding ammonia, are contained in solution along with the carbonate of lime, it is requisite to precipitate the latter by boiling, which is advantageously effected in the same vessel in which its quantity is subsequently determined. This determination is effected by treating the precipitate, suitably washed, by the method above described. With respect to the small portion which is not thrown down by boiling, an approximative account of that may be taken, admitting that each quart of water retains in solution 4 milligrms. of carbonate of lime.

If the water containing the carbonate of lime is free from other substances capable of neutralizing acids, an excess of the normal solution of acid is immediately added; and before pouring into it the alkali destined to render the portion in excess appreciable, the carbonic acid is expelled by boiling. Owing to the extreme dilution in which any uncombined acid occurs, the imperceptible quantity

which is volatilized may be neglected, and it becomes unnecessary to employ a retort. Moreover, there is nothing to prevent sulphuric acid of known strength being substituted for the hydrochloric acid. —*Journ. de Pharm.*, Oct. 1847.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On certain means of detecting the Adulteration of Flour. *By* M. Donny.

Adulteration of Flour by means of the Fecula of Potatoes.—Amongst the means of adulteration most frequently practised, that by the addition of potato fecula is the most prominent. We will therefore consider that first. The Society of Encouragement had, some time since, called the attention of chemists and bakers to this subject; and several prizes which were awarded thereon show the efforts then made in accordance with that appeal. The process for which a prize was awarded to M. Boland is founded on a property mentioned by M. Gay-Lussac, viz. that in a mixture of wheat-flour and potato-fecula, the fecula, by reason of the grains being larger, is crushed before the wheat-flour; and if at that time the mixture be washed with cold water, the liquor on being run off will be coloured blue by the presence of iodine; whilst under the same circumstances pure flour produces a liquid which will not be affected by iodine. The modification of M. Boland consists in separating by known means the gluten of the flour to be examined, and in triturating the mixture of starch and fecula resulting from such separation. Although this process appears very simple, it requires, in order to perform it properly, a certain knack, which can only be acquired by practice; for instance, the form of the mortar or pestle, their degree of smoothness, and the pressure of the hand working them, and also the time of the operation, may modify the result in such a manner, that, if the trituration be not continued long enough or strongly enough, the fecula may not be crushed; while, on the contrary, if too violent, or continued for too great a length of time, the wheat starch may be affected, and thus the fecula will erroneously be supposed to exist.

M. Donny proposes another plan for detecting this adulteration, which is by inspection through a microscope or a simple convex lens. The grains of fecula are, as is well known, of much greater diameter than those of wheat and other grain. This difference is not however sufficiently great to ensure the detection of fecula in wheat flour if the mixture has been well made. In questions of this nature, interesting to public health, and involving nearly always the fortune and honour of some citizens, only those results must be accepted which leave no doubt as to their correctness.

For this purpose M. Donny has taken advantage of an observation made some time ago by M. Payen, whose numerous indefatigable exertions have thrown such a light upon the chemical history of

starch, and the various arts in which that natural product is employed. This observation consists in the fact, that a weak solution of potash, which has no visible effect upon starch, possesses nevertheless the property of swelling the grains of fecula and considerably increasing their volume. The solution employed by M. Donny is made with 1 grm. 75 centigrms. of caustic potash dissolved in 100 grms. of distilled water, and consequently contains about 1·60° of alkali. His method of proceeding is as follows:—The flour to be examined being placed upon a plate of glass, is diluted with the above solution and inspected through the microscope; the grains of fecula may then be easily detected by their great size compared to the starch, which is not affected by the solution. The operation may be rendered still more certain by adding iodized water to the mixture after being well-dried from the solution, as the blue tint which will be assumed by the fecula will render the same more apparent. The difference caused by this process is so great that it is impossible to be mistaken, the grains of fecula being by the solution increased to a size about fifteen times as big as the starch.

This process is without doubt the most simple and most certain of any we are acquainted with; it allows an infinitely small quantity of fecula to be detected in the flour; 1 gr. even might be discovered if sufficient time and pains were bestowed upon it. This process is also applicable to the discovery of fecula in bread itself. For this purpose it is only necessary to take a small quantity of the crumb, and wet it through with the solution of potash; a portion of the liquid is then squeezed out, and placed under a lens; on inspecting it, grains of fecula will be discovered by their having swelled con siderably; they are however more difficult to distinguish by their being misshapen by being baked; but on drying and treating them with iodine, the detection will be made with the same facility a when flour is operated upon.

Mixture of Wheat-Flour with Leguminous Flour.—The leguminous substances which when pulverized are most commonly employed for adulterating wheat-flour are peas, haricot-beans, horse-beans, &c. It may be remarked that the presence of these substances, when in any quantity, cause a smell which renders their detection easy; some of them, such as haricot-beans, will not combine in the making of bread, and cannot therefore be employed to any extent. Pease-meal will not generally mix well with wheaten flour, and an eye somewhat experienced will easily detect the mixed flour from its green appearance. All these leguminous meals contain a peculiar substance called *legumine*, which is soluble in water and may be precipitated by acetic acid (vinegar). The result of the presence of this matter is, that if the meal of peas or haricot-beans be treated with cold water, and a little acetic acid be added to the liquor, it becomes thick, and a white substance (which is legumine) is precipitated; on the contrary, flour from wheat and other species of corn not containing any legumine furnish, on being treated with cold water, and when free from adulteration, a solution which will not furnish any precipitate on being treated with acetic acid. This property has been taken advantage of in order to distin-

guish fine flour from that which may have been adulterated with the above-mentioned substances. The process would be quite perfect if it were proved that in consequence of reactions, which cannot always be foreseen, the gluten or other nitrogenous matters peculiar to Cereals might not be rendered soluble in water, and partially precipitable by acetic acid. What authorizes the doubt on this point is, the difference of opinion existing amongst chemists who have tried this process.

Whatever may be the case, the following is the method proposed by M. Donny, and its efficacy has been proved. This method is founded upon the fact that the flour of leguminous substances always contains portions of cellular tissue, which may be discovered by means of a lens or microscope. In order to expose to view this tissue (which is reticulated, and consists of hexagonal meshes, and may be easily recognised when once seen). M. Donny, after having placed a small quantity of the adulterated flour on the object-bearer, dilutes it slightly with a solution of potash of such a strength as to dissolve the fecula without touching the tissue. By this means the tissue is laid bare, and its form will be very evident; and if the leguminous flour amounts only to 3 or 4 per cent., it may be discovered with certainty. The only point which requires attention is, to take care not to agitate the mixture too much while on the object-bearer, for the cellular tissue might thereby be disintegrated, and the operation would thus be rendered much more difficult.

Flour of Vetches or Horse-Beans.—These two substances, besides possessing the peculiar characteristics possessed by leguminous substances as above mentioned, and which would be sufficient to distinguish them, have another peculiar feature, which has not yet been discovered in any other substances. This peculiar feature, which was discovered by M. Donny, has been applied by him with perfect success in detecting the presence of these two substances in flour or other mixture. For this purpose, the flour is exposed first to the action of the vapour of nitric acid, and afterwards to that of ammonia; the result of which is that the bean-meal will be turned a purple colour, whilst the others will assume a yellowish hue. The following is the method of conducting the experiment:—1 or 2 grms. of the flour to be tested are placed in a small porcelain capsule of from 2 to 3 inches in diameter, which is slightly wetted in order to make the flour adhere to the sides, leaving the bottom empty; and in this empty space a small quantity of nitric acid is placed, so as not to be in immediate contact with the flour. The capsule is then covered with a small glass disc, and slightly heated by means of a spirit-lamp. The acid becomes vaporized, and acts upon the flour, causing it to assume a yellow tint. This tint is however not uniform, it being deeper at the lower part nearest the acid, and getting gradually lighter towards the top. The operation must be stopped whilst the top edge is still white, and before it has been sensibly affected by the nitric acid; the nitric acid which remains is then thrown away and ammonia substituted; the operation is then left to itself, and a ring of a bright red colour will be formed around the middle of the capsule, *i. e.* in that part where the action of the acid

has neither been too strong nor too weak. As was before observed, under the same circumstances pure wheat-flour becomes yellow.

If a mixture of the two flours be operated upon, a pink tint will be produced in depth proportioned to the quantity of bean-meal. The colour, which is doubtful to the naked eye, is very clearly seen under the lens or microscope, the tint being produced, not by a uniform colouring of the mass, as might be imagined, but by the presence of a certain number of coloured particles consisting of grains of a deep red colour, disseminated in a white or slightly yellow mass, which renders their detection very easy and certain. By this means 4 per cent., and even a less quantity, of bean-meal in wheaten flour may be detected; and vetch-flour may be discovered by the same method.

Horse-bean meal is, of all leguminous substances, that which seems to mix best with wheaten flour; it gives greater tenacity to the dough, but imparts to the bread a disagreeable gray colour; it has been employed some time by some of the Paris bakers, for the purpose of turning the bread, that is to say causing it to separate easily from the peel when put into the oven, and also to give the upper crust the reddish-brown colour so much liked, which is caused by a portion of the flour becoming candied.

The red colour which the bean-meal assumes, in consequence of the reactions above described, allows it to be detected in bread; for this purpose a portion of the crumb is taken and macerated in cold water for two hours; it is then thrown into a sieve, and the liquor which runs from it is allowed to settle, and divides into two strata; the upper stratum is then removed and carefully evaporated, and the residuum is partially dissolved by alcohol; after which the alcoholic solution is evaporated. The residuum of this evaporation, which must be carefully spread upon the sides of the capsule, is submitted to the successive action of the vapours of nitric acid and ammonia; and under the action of these reagents the residuum will assume the characteristic red colour of bean-meal. Vetch-meal may be discovered in a similar manner.

Maize and Rice-Flour.—Rice-flour could only be added to wheat-flour in particular cases, but the flour of maize is frequently used for that purpose. Maize and rice-flour may be distinguished from wheat-flour by the fact of their presenting under the microscope angular surfaces, which are not seen in the latter; these fragments are produced by portions of the husk, which is hard in rice and maize, while it is always pulverulent and farinaceous in even the hardest kind of wheat. When any suspected flour is to be tested, M. Donny advises the gluten to be first separated, by ordinary mechanical means, to collect the starch, and submit it (especially the coarser portion, which is most quickly precipitated in water) to microscopic inspection, which immediately shows the angular fragments above mentioned. It is generally advisable, for this purpose, to have a lens of small magnifying power only, which will more clearly show the difference between the fragments in question and the grains of starch.

Buck-Wheat Flour.—Buck-wheat flour, like the preceding, pre-

sents angular masses, which result from the agglomeration of grains of starch set closer together; these masses may be easily detected in a mixture of buck-wheat with the best wheat-flour; for this purpose it is only necessary to separate the gluten, and take the thickest part of the starch, which is to be submitted to the microscope. The general form of these fragments is prismatic, and similar to what is called in commerce "needle-starch."

These three latter kinds of flour, maize, rice and buck-wheat, are rough to the touch, the same as potato-fecula; they have not that softness and unctuosity possessed by wheat-flour, which property is diminished by adulteration.

Linseed-Meal.—One method of adulteration, which would scarcely have been thought of, but which has been extensively practised in Belgium, consists in adding linseed-meal to flour of grain, but more particularly rye. Linseed-meal, on examination through the microscope, may be distinguished by the presence of small fragments (generally square), of a red colour, of nearly uniform size, and very small (smaller than the grains of starch). These fragments, which are not perceptible when the grain has been previously deprived of its husk, appear, from this circumstance and their peculiar colour, to belong really to the husk of the grain; their square form and uniform dimensions show that these fragments are not the accidental result of mechanical trituration; this regularity of form depends on a circumstance which it will not perhaps be uninteresting to examine. If a mixture of flour containing linseed be treated with a solution of potash containing from 10 to 14 per cent. of alkali, the starch will be dissolved, and the fragments above mentioned will remain distinctly visible, notwithstanding their small size, in the midst of a mass of a yellowish-white colour, the linseed appearing of a reddish-brown colour. This substance may, by means of potash, be detected in bread, even if the flour from which it was prepared only contained from 2 to 3 per cent. For this purpose it is only necessary to crumble a piece of the crumb into small pieces, steep it in the solution of potash, and examine the liquor resulting from it.

The facts made known by M. Donny solve a very difficult problem, which has long occupied the attention of chemists and manufacturers, to whom it furnishes certain and easy means of detecting, and consequently preventing, the frauds most commonly practised with regard to flour of various kinds.

M. Donny's processes are especially valuable, from the degree of certainty of their effect, which indeed is almost infallible, and constitutes their most prominent feature, and which was precisely what was most wanted in these experiments; there is no guessing or supposition on the part of the operator, for he either sees or does not see the fecula, the cellular tissue, the red fragments, &c. In the former case, he states the result with certainty; in the latter, if he has any idea that something has escaped him, he leaves the investigation to a more skilful or more patient operator.—*Bulletin de la Société d'Encouragement*; as inserted in Newton's *London Journal*, Nov. 1847.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Harmaline and Harmine. By J. FRITZSCHE.

THE author, as observed on a former occasion*, has discovered in the seeds of *Peganum Harmala* a second base along with harmaline, to which he has given the name of harmine. He likewise obtained the latter as a product of the decomposition of harmaline, and its preparation has been pointed out under the bichromate of harmaline. When that salt is heated to 248°, a violent reaction suddenly occurs, which extends through the whole mass; a portion of the harmine formed is volatilized by the heat set free in this process, on which account the operation must be made in a flask, and at the same time protected as much as possible from access of air, that the porous chromiferous mass may not take fire. The white vapours of harmine adhere in icy arborescences to the upper parts of the vessel. The contents of the flask are extracted either with boiling spirit or by digestion with water containing muriatic acid; the chromiferous mass is insoluble in both liquids; the former yields harmine immediately on distillation, the latter on treatment with ammonia or potash. But in this manner only a small quantity is ever obtained; in one quantitative experiment 25 per cent. of harmine and about 65 per cent. of a dark substance, which requires further examination, was obtained. No gaseous products are formed.

The following method is far better adapted to the preparation of harmine, and yields a much larger product. When nitrate of harmaline is mixed with muriatic acid and alcohol, or such a mixture with harmaline and nitric acid brought together, and heated until the liquid, owing to the production of æther, begins to boil, there is simultaneously with the reaction of the nitric acid upon the alcohol a transformation of the harmaline into harmine. This metamorphosis is very rapidly effected; and on cooling the vessel in which the operation was performed, an abundant crop of muriate of harmine separates in very minute acicular crystals. The salt is washed with dilute muriatic acid, in which it is very sparingly soluble, and is then dissolved upon the filter in cold water to free the liquid from a resinous body, and the solution of harmine precipitated with potash or ammonia. Now in order to obtain the harmine perfectly

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pure, whether it is prepared from the Harmala seeds or from harmaline, several plans may be adopted. The harmine is separated from any admixture of harmaline by warming it with alcohol, and then adding just so much muriatic acid as is requisite to dissolve the substance, upon which the solution is retained for some time at nearly a boiling temperature with animal charcoal. So much ammonia is added to the filtered liquid that the whole of the harmine is precipitated. When cooled quickly and agitated, it separates immediately, while the harmaline requires considerable time to crystallize. The same operation may be repeated with the harmine, or it is merely dissolved in alcohol, when on slow cooling it separates in perfectly colourless crystals several lines in length. If, on the other hand, it is required to purify harmine which is perfectly free from harmaline, it is dissolved in water to which a little sulphuric acid has been added, the solution is boiled with charcoal immediately, or after the sulphate of harmine has been converted, by the addition of chloride of sodium, hydrochloric acid, nitre or nitric acid, into muriate or nitrate, the solution filtered, and the separated salt collected, which is again dissolved in water and precipitated with dilute ammonia. The harmine separates in acicular crystals, which are very hard, brittle, shining, and highly refractive; their form is a four-sided rhombic prism. They may be obtained from alcohol half an inch and more in length. With respect to solubility in water, harmine behaves very similarly to harmaline; once separated, it is, if not quite insoluble, very sparingly soluble indeed; but on precipitating it from solutions of its salts, a portion always remains dissolved. It is tasteless, while its salts, like those of harmaline, have a somewhat bitter taste. When separated by an alkali from its salts, it appears at first in minute oily drops, which congeal to a crystalline mass, slowly in cold but very quickly in hot water. Harmine does not dissolve so readily in alcohol as harmaline, which is the reason of its separating more quickly from hot saturated solutions, nor does it experience any alteration in this solution from the access of air. Harmaline is somewhat soluble in æther, which does not throw down any harmine from the alcoholic solution. Oil of lemon, oil of turpentine and olive-oil dissolve a large quantity of harmine, naphtha but little, without these oils being altered by boiling or preservation. Harmine expels ammonia from salts of ammonia less easily than harmaline; indeed it behaves altogether like a weaker base. The salts of harmine are colourless, yellowish when not perfectly pure; their solutions are yellowish in the concentrated state, and exhibit on greater dilution a bluish tint; this is particularly the case with alcoholic solutions by reflected light. On analysis harmine yielded the following results:—

Carbon	74·38	73·89	74·61	74·19	27	= 2028·24	74·35
Hydrogen ..	5·53	5·32	5·77	5·60	12	149·76	5·49
Nitrogen	13·02	..	..	..	2	350·12	12·83
Oxygen	7·07	..	..	..	2	200·00	7·33

The empirical formula for harmine is consequently $C^{27}H^{12}N^2O^2$,

and the rational formula, if it is regarded as a conjunct ammonia, $= C^{27} H^9 NO^2 + NH^3$, according to which it contains the same elements as harmaline less 2 equivs. of hydrogen.

Chloride of Platinum and Harmine, $C^{27} H^9 NO^2 + NH^4 Cl + Pt Cl^2$. —When a cold solution of muriate of harmine, to which some muriatic acid has been added, is treated with chloride of platinum, a flocculent precipitate results; but if the compound is heated in the liquid, or precipitated from a hot solution of the muriate of harmine, it is crystalline. The substance, dried at 248° and burnt with chromate of lead, after careful drying furnished—

Carbon	37·90	27 =	2028·24	38·25
Hydrogen	3·17	13	162·24	3·06
Nitrogen	..	2	350·12	6·60
Oxygen	..	2	200·00	3·77
Chlorine	..	3	1329·84	25·08
Platinum	23·25	1	1232·08	23·24

Muriate of harmine likewise affords with perchloride of mercury a sparingly soluble double salt, which separates from hot solutions like the preceding salt, but in flakes from a cold solution.

Muriate of Harmine.—Harmine, dissolved in water by the aid of muriatic acid, separates almost completely on the subsequent addition of an excess of muriatic acid, because this salt, like the muriate of harmaline, is insoluble in muriatic acid. When dried in the air, great care being taken to prevent the access of ammoniacal vapour, it contains 4 atoms or 12·38 per cent. of water of crystallization, and is of a yellowish colour; at 212° the water escapes, and the salt becomes white. From strong alcohol it separates immediately anhydrous, but on evaporating the alcohol becomes coated with a yellowish layer of hydrated salt from the fixation of water. The yellow hydrated salt is obtained from weak spirit. Muriate of harmine dissolves pretty abundantly in alcohol and in pure water at the ordinary temperature, but far more so in the hot liquids, so that it can be recrystallized. The following results were obtained on analysis:—

	Air-dried.
Water	12·43
Salt	87·57

	Dried at 230° F.			
Harmine	83·80	83·66	84·44	84·83
Muriatic acid	14·30	14·23	14·14	14·43
Loss	1·90	2·11	1·42	0·74

The loss of harmine is owing, as is the case with harmaline, to its not being entirely precipitated by ammonia; however, the numbers found for the muriatic acid and water agree closely with the formula $C^{27} H^9 NO^2 + NH^4 Cl + 4HO$. To verify this, the quantity of muriate which a weighed amount of harmine would afford was ascertained. For this purpose it was dissolved in a little water and muriatic acid, precipitated with muriatic acid, and collected upon a

weighed filter; it had increased 14·23 per cent., which agrees therefore with the above numbers.

Sulphate of Harmine.—Sulphuric acid forms a neutral and an acid salt with harmine. The first is obtained when dilute sulphuric acid is digested with an excess of harmine, the latter when harmine is dissolved in boiling alcohol containing an excess of sulphuric acid. The neutral salt separates in a crystalline state on concentrating its solution; but, once separated, it dissolves with far more difficulty in water, but can be obtained from alcohol in very perfect crystals. It contains two atoms of water of crystallization, which escape at 230°. The crystals of the acid salt are very similar, but they are anhydrous. The neutral salt yielded on analysis 6·57 per cent. water of crystallization in the air-dried state, and 15·14 per cent. sulphuric acid when dried at 230°. The formula $C^{27} H^9 NO^2 + NH^4 O, SO^3 + 2HO$ requires 6·31 water and 14·98 sulphuric acid. The acid salt afforded 25·59 per cent. sulphuric acid; the formula $C^{27} H^9 NO^2 + NH^4 O, SO^3 + HO\ SO^3$ requires 25·32.

Oxalate of Harmine.—The neutral salt is obtained when recently-precipitated harmine is added to a boiling solution of oxalic acid until a crystalline precipitate separates, which is very sparingly soluble in water, and was not further examined. The acid salt separates from aqueous solutions of harmine in excess of oxalic acid in fine fasciculate crystals, which were found to contain 5·67 per cent. water of crystallization; the formula $C^{27} H^9 NO^2 + NH^4 O, C^2 O^3 + HO$, $C^2 O^3 + 2HO$ requires 5·52. On burning the anhydrous salt dried at 230°, there was found—

Carbon	60·18	31	= 2328·72	60·43
Hydrogen	4·58	14	174·72	4·53
Nitrogen	..	2	350·12	9·09
Oxygen	..	10	1000·00	25·95

Chromate of Harmine.—The author could not determine with certainty whether a neutral chromate exists. On mixing a solution of neutral chromate of potash with muriate of harmine, it behaves like pure potash; and when warmed, white harmine separates. In the cold a syrupy mass separates, which solidifies after some time; but this perhaps is only a mixture of harmine with the bichromate of harmine. The bichromate of harmine is always formed when acid solutions of harmine are mixed with chromic acid or chromates. The salt separates in oily drops, which soon solidify, and behaves in this, as in many other respects, very similarly to harmaline; it is sparingly soluble in cold, more abundantly in hot water. In alcohol of moderate strength it dissolves at the boiling-point unaltered, and in considerable quantity; at a higher temperature decomposition suddenly takes place, a portion of the base is volatilized unaltered, and another new alkaloid, which will be subsequently described, is produced. For analysis, a carefully crystallized salt, obtained by pouring an acid solution of acetate of harmine into a solution of chromic acid containing acetic acid, was employed. The salt is represented by the formula $C^{27} H^9 NO^2 + NH^4 O + 2CrO^3$, as the following numbers show:—

Carbon.....	48·53	49·33	48·92	27	=2028·24	49·49
Hydrogen	3·93	3·85	3·78	13	162·24	3·96
Nitrogen	..	..	..	2	350·12	8·54
Oxygen	..	..	..	6	600·00	14·64
Chromic acid ..	23·48	24·23	23·84	1	957·74	23·37

Acetate of Harmine.—Acetic acid dissolves a large quantity of harmine, but a gentle heat suffices to separate the acetate again into its constituents, whence on every evaporation, with the assistance of heat, harmine separates before any acetic acid escapes; and on evaporation to dryness the solution leaves pure harmine free from acetic acid. This behaviour may be advantageously turned to account for distinguishing and partially separating harmaline from harmine. *Nitrate of harmine* is obtained by saturating harmine with nitric acid or precipitating acetate of harmine with dilute nitric acid or with the solution of a nitrate; it is sparingly soluble in cold water, and still more sparingly in water containing nitric acid. The nitrate of harmine separates much earlier from a solution of the nitrates of harmaline and harmine, so that these salts may be separated in this manner. *Carbonate of harmine* does not probably exist: at least pure harmine was precipitated from its solution by the addition of bicarbonate of potash. *Hydrobromate* and *hydriodate* of harmine are obtained by precipitating a solution of acetate of harmine with one of an alkaline bromide or iodide, when these salts separate in a crystalline state. They resemble very closely the muriate in their behaviour. *Hydrocyanic acid* could not be combined directly with harmine, but harmine enters into some double cyanides. Ferrocyanide and ferridcyanide of potassium produce precipitates in solutions of salts of harmine; that with the first salt, according to whether the solutions were hot or cold, being in yellow or orange crystals of different form; that with the latter salt flocculent and dirty yellow in the cold, becoming brick-red and crystalline on boiling. *Sulphocyanide of harmine* is obtained by precipitating a dilute solution of muriate of harmine with sulphocyanide of potassium, in the form of a dazzling white precipitate, consisting of a tissue of very minute acicular crystals. As this salt is very soluble in hot water, but sparingly so in cold, it is obtained unaltered from the hot saturated solution on cooling. On mixing a solution of a salt of harmine with the hydrosulphate of ammonia, no combination of it with sulphuretted hydrogen is obtained as with harmaline, but pure harmine separates just as if its salts were treated with pure ammonia.—*Bulletin de St. Pétersburg*, vol. vi. p. 242.

On the Behaviour of the Deutoxide of Nitrogen towards Iodine, Chlorine, Bromine and Oxides. By Prof. Schönbein.

The author is of opinion that the normal nitrites have the composition $RO^2 + NO^2$; the formulæ of the nitrite of lead and protonitrite of manganese would accordingly be $PbO^2 + NO^2$ and $MnO^2 + NO^2$, that is, compounds of the hyperoxides of lead and

manganese with deutoxide of nitrogen. If we attempt to prepare such compounds in a direct manner, by bringing together the constituents mentioned, as for instance suspending finely lævigated peroxide of lead or manganese in water deprived of air, and agitating the mixture in well-stoppered bottles with deutoxide of nitrogen, both the deutoxide of nitrogen and the peroxide disappear, and the water is then found to contain a nitrite in solution. The peroxide of lead combines much more rapidly with the deutoxide of nitrogen than the manganese, and with the latter long-continued agitation is requisite to prepare any quantity of the compound. Minium and the brown oxide of manganese likewise yield nitrites with deutoxide of nitrogen, and in both cases white precipitates of hydrated oxide and protoxide separate.

When oxide of silver is agitated with water and deutoxide of nitrogen, metallic silver separates, and at the same time nitrite of silver is produced. Oxide of gold, treated in the same manner, is quickly reduced, and the water contains nitric acid. Peroxide of hydrogen, agitated with a suitable proportion of deutoxide of nitrogen, furnishes nitric acid. If iodine, finely divided in water, is shaken with deutoxide of nitrogen, hydriodic and nitric acids are formed; but only a small amount of these two bodies can be produced in this manner, because they can only coexist in a very diluted state; and all further action of the iodine upon the gas must cease as soon as the two acids have been produced in such quantities as to begin to react upon one another. Highly-coloured bromine-water behaves toward the deutoxide of nitrogen like iodine-water, only that more hydrobromic and nitric acids are produced than in the case of iodine. When chlorine-water is shaken with a sufficient quantity of the deutoxide of nitrogen, nitric and muriatic acids are obtained.—*Journ. für Prakt. Chem.*, xli. p. 225.

On a new Product of Decomposition of Urea.
By M. Wiedemann.

Pelouze has asserted that nitrate of urea is decomposed at about 284° into nitrate of ammonia and urea, with evolution of carbonic acid and nitrous oxide; further, that at a higher temperature the nitrous oxide disengaged from the nitrate of ammonia decomposes the cyanuric acid formed from the urea, and that in its place a small quantity of a new acid occurs, which dissolves with difficulty in water, and is precipitated by basic acetate of lead. The author did not succeed in preparing this acid; he always found among the products of decomposition of nitrate of urea more or less cyanuric acid; he discovered, however, on heating nitrate of urea, as also pure urea, a new body, for which, considering its composition, he proposes the name of *biuret*. It is easily soluble in water and alcohol, crystallizes from the former with 2 equivs. water, which it parts with at 212°, and from alcohol anhydrous. Its composition is represented by the formula $C^4 H^3 N^3 O^4$.

Biuret dissolves unaltered in sulphuric acid, and is destroyed only

by long-continued boiling in it; it is not precipitated from its solutions by bases, acids or metallic salts, and is, as far as the author is able to judge from his experiments, a neutral substance. It is especially characterized from its solution acquiring an intensely red colour on the addition of caustic potash and solution of sulphate of copper.

It fuses when heated, and is converted with loss of ammonia into cyanuric acid,

$$3C^4H^5N^3O^4 - 3H^3N = 2C^6H^3N^3O^6.$$

Now it is easily seen from the composition and preparation of biuret, that for its formation the urea need only part with ammonia,

$$2C^2H^4N^2O^2 - H^3N = C^4H^5N^3O^4.$$

The urea appears to be first converted on the application of heat into biuret, and this then into uric acid. If we regard urea as cyanate of ammonia, $C^2HNO^2 + H^3N$, biuret may be considered as bicyanate of ammonia, $2C^2HNO^2 + H^3N$. Or admitting with Berzelius oxide of urene instead of cyanic acid in urea, and representing it by $UrO^2 = C^2HNO^2$, then urea is UrO^2Ar, and biuret $2UrO^2, Ar$.

On the Conversion of Tannic into Gallic Acid.
By C. Wetherill.

The following experiments were made with a view to ascertain whether a substance is contained in tannic acid which constitutes this acid when conjoined with gallic acid. The author is led from his investigation to regard tannic as isomeric with gallic acid dried at 212°, and to derive the latter from it by the fixation of water. The tannic acid used in the experiments was prepared according to Pelouze's method, and was purified by solution in spirit, and subsequently in water. It was white, and was perfectly precipitated from its solution in water by sulphate of quinine, so that the liquid filtered from the precipitate was no longer coloured by persalts of iron. Of the different substances examined, sulphuric acid appeared to effect the conversion of the tannic acid best. If 50 grms. of dry tannic acid are heated to boiling in a mixture consisting of 100 cubic centimetres sulphuric acid of 1·84 spec. grav. and 400 cubic centimetres water, there will be found in the course of a few days an abundant precipitate of very white gallic acid. Once, on employing this process, the sulphuric acid was removed by means of carbonate of baryta, the liquid filtered, evaporated to dryness, weighed, treated with æther, and again weighed, and the solution acidified with acetic acid, treated with basic acetate of lead, the liquid filtered, and again precipitated with basic acetate of lead. This last precipitate was well washed and decomposed with sulphuretted hydrogen, after which the filtered solution was treated as above. In the first treatment, 12 per cent. of a substance insoluble in æther was obtained, which consisted principally of gallate of baryta, and of 1 to 2 per cent. of a black body, which was probably an impurity in the tannic acid. The precipitated

sulphate of lead, and likewise the sulphate of baryta, also parted with gallic acid to nitric acid; but excepting the above-mentioned black substance, nothing further could be detected; and it therefore appears that the entire amount of tannic acid was in the above manner converted completely into gallic acid. Lime might be substituted for the baryta with the same result. The maximum quantity of gallic acid obtained amounted to 87·4 per cent. of the tannic acid. In an analysis of tannic acid, the author arrived at the generally admitted formula $C^{18}H^{5}O^{12}$; it yielded 50·63 carbon, 3·64 hydrogen, and 45·73 oxygen. Wackenroder and Larocque have stated that this conversion may also be effected by ferments, albumen, blood, and a substance capable of fermentation in gall-nuts; and Humfeld found that tannic acid was destroyed without the formation of gallic acid, by the action of oxidizing agents, such as manganese, chromic acid, peroxide of mercury, &c. If the results of the analyses of gallic acid dried at 212° are compared with those of tannic acid, it appears, as above stated, that the former is derived from the latter by the fixation of water. We have—

	Gallic acid according to Pelouze.			Tannic acid.		
Carbon ..	49·56	7	= 49·41	50·63	18	= 50·93
Hydrogen	3·70	3	3·53	3·64	8	3·79
Oxygen ..	46·74	5	47·06	45·73	12	45·28

These numbers do not differ much from one another; and if we bear in mind that tannic acid is uncrystallizable, and that a slight impurity of one of the substances is sufficient to produce the above differences, and moreover that tannic acid is bibasic, we may perhaps represent gallic acid by $C^{7}H^{3}O^{5}$, and tannic acid by $2(C^{7}H^{3}O^{5})$ or $C^{14}H^{6}O^{10}$. Crystallized gallic acid is then derived from the latter by the assimilation of water.—*Journ. de Pharm.*, xii. p. 107.

On Lactic Acid and its Salts.
By H. Engelhardt *and* R. Maddrell.

The lactic acid employed in the following experiments was prepared in large quantity according to the process of Bensch*. The use of lump-sugar instead of the brown kind yields a white lactate of lime on the first crystallization. When the latter has been entirely freed by frequent recrystallization from the nitrogenous substance which tenaciously adheres to it, pure lactic acid can be easily prepared from it. For this purpose the lactate of lime is decomposed by an insufficient quantity of sulphuric acid, so that some of the salt is left undecomposed, and the liquid contains no free sulphuric acid. The aqueous lactic acid separated from the gypsum is evaporated to a syrup, and this treated with æther, in which the acid dissolves in every proportion, while the undecomposed salt, gypsum, &c., remain behind. If the acid is prepared from its zinc-salt by decomposing this with sulphuretted hydrogen, the evaporated acid

* Page 206 of the present volume.

to be pure must be equally dissolved in æther, in order to separate those lactates of bases which usually contaminate the carbonate of zinc. Wackenroder's view, that on using a ferment containing no fat only lactic acid and no butyric acid is formed, is not adopted by the authors, who cannot admit the production of butyric acid to be caused by the fat of the caseine; because when pure lactic acid is saturated with pure carbonate of lime, and the solution of this salt exposed with caseine free from fat to those conditions favourable to the formation of butyric acid, the lactic acid is very soon converted into butyric acid. Moreover, the twice recrystallized lactate of lime, which was free therefore from fat but not from nitrogenous matter, soon passed into the butyric fermentation; consequently the formation of these two acids is successive, and not contemporaneous. The amount of nitrogenous substance requisite to convert lactic into butyric acid is remarkably small, so that the authors even made one experiment to ascertain whether perfectly pure lactate of lime did not pass over into the butyrate; but not a trace of butyric acid was found in it after it had been exposed for six weeks to a temperature of 86° F. Access of air appears to accelerate the conversion of lactic into butyric acid, but not to be requisite, for the reaction took place in a closed flask provided with a glass tube just as well, only more slowly; and the collected gas consisted of carbonic acid and hydrogen in the proportion of three of the first to four of the latter, as required by theory. That mannite and a gummy substance are formed with the lactic acid is confirmed by the authors only as regards the latter substance. After evaporating the lyes from the lactate of lime to a syrup, boiling alcohol dissolves a large portion of the residue; and on cooling, considerable quantities of a crystalline mass separate, which does not however consist of mannite, but is a peculiar lime-compound. It dissolved in hot absolute alcohol, in which the lactate of lime is almost insoluble, and yielded on analysis numbers leading to the formula $CaO, C^{50} H^{14} O^{14} + 12HO$; the 12HO escape already *in vacuo*. This substance was not further examined; but after separating the lime it did not possess the least sweetish taste.

Pure lactic acid obtained according to the above method has always a somewhat brownish colour. It dissolves in water, alcohol and æther, imparting to these liquids a pure acid taste, and remains unaltered in its solutions. At $-4°$ to $-12°$ F. it does not become solid. All the lactates are insoluble in æther, and sparingly soluble in alcohol and cold water; boiling alcohol does not dissolve much more than cold, but boiling water readily dissolves them. Most of the salts bear a temperature of 302°–338°, some even of 410°, without experiencing any change. All the salts that were obtained crystallized were permanent in the air, and several, for instance the zinc, iron and cobalt-salts, remained constant even over sulphuric acid. They all part with water of crystallization *in vacuo*. The majority of the salts crystallize, but only those of copper and manganese could be obtained in well-developed crystals.

Lactate of Silver.—This salt is formed when carbonate of silver

is boiled with lactic acid. If an excess of the carbonate has been employed, the solution is perfectly neutral; and if not too dilute, the silver-salt subsequently separates in silky needles, which soon blacken by exposure to light, especially at a high temperature. The lactate of silver dissolves very readily in hot alcohol, while it is nearly insoluble in cold; consequently a hot saturated alcoholic solution congeals on cooling to a magma of crystals. When the aqueous and alcoholic solution is boiled for some time, the liquid acquires a blue colour, and very soon afterwards brown flakes separate. Æther entirely precipitates the silver-salt from the alcoholic solution. It bears a temperature of 176°, but is decomposed at 212°, becoming brown and disengaging gas. The salt for analysis was frequently recrystallized from water, then precipitated from the aqueous solution with alcohol, and dried after the alcohol had been removed by means of æther. I. is the analysis of the salt dried at 176°, II. that of the salt dried *in vacuo*:—

	I.	II.		
Carbon	18·07	18·05	6	18·27
Hydrogen	2·53	2·85	5	2·54
Oxygen	20·84	20·94	5	20·31
Oxide of silver	58·56	58·16	1	58·88

The air-dried salt lost at 176° 7·83–8·85 per cent. water, which quantity corresponds to 2 equivs., which require 8·37 per cent.; hence the formula of the air-dried salt is $AgO, C^6 H^5 O^5 + 2HO$, and that of the salt dried *in vacuo* and at 176° = $AgO, C^6 H^5 O^5$.

Lactate of Copper is obtained by precipitating lactate of baryta with sulphate of copper, and by boiling carbonate of copper with lactic acid; but in the latter case basic salts are easily formed besides the neutral one; the latter is obtained in both ways in large well-developed crystals, which exhibit all the tints of green to blue. The green salt cannot be converted into the blue modification by recrystallization. The crystals are tabular-prismatic, and possess considerable resemblance to those of gypsum. When some alcohol is added to the aqueous solution of the salt, the crystals differ so much in appearance that they might be regarded as distinct from those crystallized from water, which however, as regards its composition, is not the case. The colour of the salt crystallized from the solution to which alcohol had been added is much lighter than that from water. The copper-salt dissolves in 6 parts cold and 2·2 parts of boiling water, in 115 parts cold, and 26 parts boiling alcohol. Its solution has a strong acid reaction; it may be heated to 320° without experiencing any change, which occurs at 410° with ignition of the salt. The following analysis shows its composition:—

Carbon	29·56	29·71	6	28·82
Hydrogen	4·07	4·22	5	4·14
Oxygen	34·11	33·79	5	33·13
Oxide of copper	32·26	32·28	1	32·91

Loss of water at 212° = 12·98, 12·91, 13·49, corresponding to 2 equivs., which require 12·98 per cent. The air-dried salt has consequently the formula $CuO, C^6 H^5 O^5 + 2HO$.

Basic salts of copper are obtained when, as previously stated, carbonate of copper is boiled with lactic acid. They are very sparingly soluble both in cold and in hot water, and can therefore be easily separated from the neutral salt. In the pale blue crystalline mass which separated on the cooling of the liquid, a dark heavier salt could be separated by suspension from the lighter one, and was obtained tolerably pure; it afforded 49·89 per cent. of oxide of copper, leading to the formula $2CuO, C^6 H^5 O^5$, which requires 49·52.

Lactate of Cadmium is very readily obtained by saturating lactic acid with carbonate of cadmium; it crystallizes in needles, dissolves in 10 parts cold and 8 parts boiling water, and is insoluble in cold and boiling alcohol; the solution is perfectly neutral. A boiling saturated solution of this salt does not crystallize on cooling; it must be evaporated until a film appears in order to obtain crystals. The crystallized salt is anhydrous; it lost in one experiment up to 212°, 0·277 per cent.; consequently only hygroscopic water:—

Carbon	24·79	24·64	6	24·86
Hydrogen	3·45	3·42	5	3·45
Oxygen	27·88	..	5	27·62
Oxide of cadmium	43·88	..	1	44·07

Lactate of the Protoxide of Mercury.—This salt is very easily obtained by mixing a warm solution of lactate of soda with one of the protonitrate of mercury. The mixture is at first colourless, but soon becomes rose- and afterwards carmine-coloured, and deposits some mercury, from which the liquid is filtered. In the course of twenty-four hours a very beautiful red salt separates in crystals, which are very sparingly soluble both in cold and boiling water. On boiling, metallic mercury is eliminated, and it is converted into a persalt. When cold solutions of the two salts are used, the red colour is a long time in making its appearance. The salt is insoluble in cold alcohol, very sparingly soluble in boiling, being decomposed with separation of a white powder. The solutions are strongly acid. At 212° its colour grows darker; it is however not decomposed, but parts with a quantity of water corresponding to 2 equivs. Its composition is represented by the formula $C^6 H^5 O^5, Hg^2 O + 2HO$.

Basic Lactate of the Sesquioxide of Mercury.—When the sesquioxide of mercury is boiled with dilute lactic acid until the solution is saturated, and the liquid is evaporated to a syrupy consistence, two salts separate, the one colourless and easily soluble in water, the other yellow and insoluble. The latter was not examined on account of the small quantity obtained. The soluble salt crystallizes in prisms with a strong lustre, dissolves with difficulty in cold and boiling alcohol, and is not decomposed on boiling. Its solutions have an acid reaction. The salt proved to be anhydrous, and to have the following composition:—

Carbon	12·39	12·42	6	12·11
Hydrogen	..	..	5	1·68
Oxygen	..	..	5	13·46
Sesquioxide of mercury	73·02	..	2	72·75

Basic Protolactate of Tin is prepared by mixing an acid solution of protochloride of tin with lactate of soda; it separates as a white crystalline powder, which can be washed with water, for it is entirely insoluble in cold and scarcely soluble in hot water. It is absolutely insoluble in boiling alcohol. Muriatic acid readily dissolves it, acetic acid only after long boiling. It is anhydrous, and is composed of—

Carbon	16·95	6	16·75
Hydrogen	1·96	5	2·33
Oxygen	17·75	5	18·62
Protoxide of tin	63·34	2	62·30

Lactates of Tin and Lead.—No precipitate was produced by lactate of soda in a solution of the perchloride of tin, nor in one of basic acetate of lead. On evaporating lactic acid saturated with carbonate of lead, a film of carbonate of lead separates, while the liquid acquires a faintly acid reaction. The liquid dries over sulphuric acid to a gummy mass, which is readily soluble in spirit, and cannot be obtained crystallized from it. Æther does not dissolve a trace of the lead-salt.

Lactate of the Oxide of Uranium.—Oxide of uranium, prepared by heating the nitrate to redness and exhaustion with boiling water, dissolves easily in lactic acid. The solution, after concentration, deposits the salt as a crust of yellow crystals. The solutions are decomposed by sunlight. Not a trace of the salt is dissolved by cold or boiling alcohol. The salt is anhydrous, and yielded on analysis 63·46 per cent. of oxide of uranium, leading to the formula $U^2 O^3, C^6 H^5 O^5$.

Lactates of the Peroxide of Iron, of Chromium and of Alumina.—None of these salts crystallize; the two first metals dissolve easily in lactic acid, but alumina is nearly insoluble in it; however, on decomposing sulphate of alumina with lactate of baryta, a liquid is obtained which contains a large quantity of alumina in solution.

Lactate of the Protoxide of Iron is obtained by decomposing lactate of baryta with protosulphate of iron, or according to the process of Pagenstecher, by mixing lactate of ammonia with protochloride of iron; in both cases spirit is added to the clarified solution of the salt, when it separates in minute white needles, which after drying have a silky lustre. From pure water it is obtained in tolerably large pale yellow needles; it is sparingly soluble in cold water, but soluble in boiling water and alcohol. The solutions have a strong acid reaction, and soon become dark brown in the air without depositing any basic persalt. The dry salt does not alter in the least by exposure to air, and the weight of the salt remains quite constant over sulphuric acid. Between 122° and 140° it loses water and becomes brown; if retained for any length of time at this temperature, it turns black, dissolves in this state easily in water, and reduces but little silver from a solution of the nitrate. At 248° the preceding salt, which is oxidized to the state of perlactate, evinces signs of decomposition by the diffusion of empyreumatic vapours. The proto-

lactate of iron parts with the whole of its water = 19·13 per cent., which corresponds to 3 equivs.; the analysis of the salt agrees with the formula FeO, $C^6 H^5 O^5 + 3HO$.

Lactate of Zinc was prepared by boiling carbonate of zinc with pure lactic acid. It dissolves in 58 parts of cold and 6 of boiling water, is almost insoluble in cold and in boiling alcohol; its solutions have an acid reaction. It parts with the whole of its water *in vacuo*, but with none of it over sulphuric acid. It may be heated without any perceptible change to 410°. The authors' analysis agrees with the known formula ZnO, $C^6 H^5 O^5 + 3HO$.

Lactate of Nickel is formed on boiling carbonate of nickel with lactic acid, or by mixing lactate of baryta with sulphate of nickel; it is obtained in acicular apple-green crystals, is almost insoluble in cold water, cold and boiling alcohol, is readily soluble in boiling water, and owing to these properties is precipitated from its aqueous solution by alcohol in the form of a crystalline paste. This salt experiences no alteration by exposure to the air; over sulphuric acid it loses a considerable portion of water, of which it contains 3 equivs., 2 of which escape at 212°, and the third only at 266°. The formula of the air-dried salt is NiO, $C^6 H^5 O^5 + 3HO$.

Lactate of Cobalt is obtained by boiling hydrated oxide of cobalt with lactic acid. It forms a peach-blossom red salt, very similar in other respects to the salt of nickel; it loses no water over sulphuric acid, but it does *in vacuo*. At 212° the air-dried salt lost 18·61–18·16 per cent. water; 3 equivs. require 18·55. The dry salt yielded on analysis—

Carbon	30·36	30·26	6	30·36
Hydrogen	4·46	3·89	5	4·22
Oxygen	33·69	..	5	33·79
Oxide of cobalt	31·49	..	1	31·63

Lactate of the Protoxide of Manganese is obtained on boiling protocarbonate of manganese with lactic acid in colourless or faintly amethyst-coloured crystals, possessed of considerable lustre. It is somewhat soluble in cold water, and readily so in boiling; insoluble in cold alcohol, and slightly soluble in boiling. When the aqueous solution of the salt, from which very perfect crystals may be obtained by evaporation, is precipitated with alcohol, the salt has a totally different appearance to that prepared from pure water, but exactly the same composition. The protolactate of manganese is not altered by exposure to the air; it loses over sulphuric acid a considerable quantity of water, no less than 9 per cent., and *in vacuo* about 2 equivs. The salt crystallized from water gave off 18·69 per cent. at 212°, and that which separated from water containing spirit 19·77, or in both cases 3 equivs. The formula of the air-dried salt is consequently MnO, $C^6 H^5 O^5 + 3HO$.

Carbon	30·61	6	30·84
Hydrogen	4·31	5	4·28
Oxygen	34·52	5	34·28
Oxide of manganese	30·56	1	30·60

Lactate of Magnesia is obtained on mixing lactate of baryta with sulphate of magnesia, or by boiling carbonate of magnesia with lactic acid; it is insoluble in spirit and in absolute alcohol, both hot and cold. It is entirely dissolved by 6 parts of boiling and 28 parts of cold water; the solution is perfectly neutral, and leaves on evaporation a silvery-white residue of a satiny lustre. The statement that this salt effloresces is not confirmed by the authors, for it lost nothing in weight after exposure for three weeks to the air, and even over sulphuric acid it decreased very slowly, but *in vacuo* it soon parted with water. The 21·12 per cent. water which escapes at 212° corresponds to 3 equivs., which require 21·017 per cent. The air-dried salt is represented by the formula $MgO, C^6 H^5 O^5 + 3HO$.

Lactate of Lime.—This salt was prepared by saturating lactic acid with carbonate of lime; it separates from the concentrated solution in hard spherical granules, and dissolves in every proportion in boiling water and spirit, as it melts at this temperature in its water of crystallization. Of cold water it requires 9·5 parts for solution, and is insoluble in cold spirit and in boiling absolute alcohol. The lactate of lime, which separates from the spirituous solution, has the same amount of water of crystallization as that crystallized from water. It parts with the whole of its water *in vacuo*. The salt, dried at 212°, afforded 29·23, 28·91 and 29·30 per cent., or 5 equivs. of water; it bears a temperature of 356° without decomposition. The analysis of the salt agrees with the formula $CaO, C^6 H^5 O^5 + 5HO$; consequently the statement of the authors differs from those of Wackenroder, the fifth equiv. of water not being eliminated at 356°, but with the whole of the water at 212°.

Lactate of Lime and Chloride of Calcium.—When the aqueous solution of the lactate of lime is evaporated with a large excess of chloride of calcium, this double salt separates in well-developed crystals, which are washed with cold alcohol, as this does not easily dissolve them. It is necessary to have an excess of the chloride of calcium, which can be removed by spirit, which is not the case with lactate of lime, as on repeated crystallization the double salt separates into its constituents. It dissolves readily in water and in boiling spirit; boiling absolute spirit likewise dissolves some. The air-dried salt lost at 230° 2·45 and 22·82 per cent. water, which correspond to 5 equivs. = 20·60; and yielded, when dried at 230°, numbers which lead to the formula $CaCl + CaO, C^6 H^5 O^5$, and for the hydrated salt the formula $CaCl + CaO, C^6 H^5 O^5 + 6HO$:—

Carbon	21·14	6	20·75
Hydrogen	3·45	6	3·46
Oxygen	26·79	6	27·68
Chlorine	20·75	1	20·44
Calcium	11·71	1	11·53
Lime	16·16	1	16·14

Lactate of Strontia in the air-dried state is represented by the formula $SrO, C^6 H^5 O^5 + 3HO$, and by $SrO, C^6 H^5 O^5$ when dried at

212°. The salt, dried at 212°, afforded 39·02 per cent. of strontia; theory requires 38·97; and the air-dried salt lost at 212° 17·70 per cent. water; according to theory 16·90 should have been obtained.

Lactate of Baryta is an amorphous powder, which behaves towards alcohol and æther like the lactate of lead.

Lactates of Potash of Soda and of Ammonia could not be obtained crystallized.

Bilactate of Baryta and Bilactate of Lime.—When as much lactic acid is added to lactate of baryta as it already contains, and an excess to lactate of lime, acid salts are formed in both cases. The bilactate of baryta has a strong acid reaction, forms very hard perfect crystals, is not altered by being kept over sulphuric acid or *in vacuo*, and dissolves readily in water. The bilactate of lime yields on evaporation, if there is not a very large excess of lactic acid present, at first the neutral, and subsequently the acid salt in crystals resembling wavelite, which are washed with æther to remove the free lactic acid. The analysis of the air-dried baryta-salt led to the formula $BaO, HO + 2C^6 H^5 O^5$, and that of the lime-salt, dried at 176°, to the analogous formula $CaO, HO + 2C^6 H^5 O^5$. This latter lost up to 176°, 8·80 per cent. water, corresponding to 2 equivs., so that the hydrated lime-salt = $CaO\ HO + 2C^6 H^5 O^5 + 2HO$. Both salts gave off an empyreumatic odour between 176° and 212°:—

Carbon	28·86	12	29·07	Carbon	36·20	12	36·18
Hydrogen	4·51	11	4·44	Hydrogen	5·81	11	5·53
Oxygen.....	36·16	11	35·53	Oxygen	43·99	11	44·22
Baryta	30·47	1	30·96	Lime	14·01	1	14·07

From the existence of these two acid salts, the authors regard lactic acid as a bibasic acid; its formula becomes therefore $C^{12} H^{10} O^{10} + 2HO$. In the neutral lactates both atoms of water are replaced by bases, and only one in the acid salts.—Liebig's *Annalen*, lxiii. p. 83.

On a new Acid of Sulphur. *By* J. Fordos *and* A. Gélis.

All the chlorides of sulphur yield with aqueous sulphurous acid the same compounds. The principal product of this reaction is a new oxide of sulphur, in which 5 equivs. of sulphur are combined with an equal number of equivalents of oxygen, constituting a molecule which saturates but 1 equiv. of base, and which consequently is represented by the formula $S^5 O^5$, MO.

This acid differs from all the acids of sulphur hitherto known. It cannot be confounded with that to which M. Wackenroder has assigned the same formula*, and the formation of which he observed in the reaction of sulphuretted hydrogen upon aqueous sulphurous acid; since he states positively in his paper that the barytic salt which he obtained dissolves in alcohol and in æther, and cannot be precipitated from its aqueous solution by these agents, which is exactly the method we adopt to isolate our acid.

* Chem. Gaz., vol. iv. p. 465.

The new acid $S^5 O^5$, MO is isomeric with hyposulphurous acid $S^2 O^2$, MO; both, in fact, have the same centesimal composition, but they differ completely in all their characters. Mineral chemistry offers no case of isomerism comparable to that of these two acids: for analogous cases we look among the compounds of carbon, and this fact supports the approximation which Berzelius was the first to establish between the composition of the recently-discovered acids of sulphur and that of the compounds of organic chemistry.

In our memoir we divide all the acids of sulphur into two distinct classes; in the one the sulphur remains invariable, and the quantity of oxygen increases; in the other the number of equivalents of oxygen being 5, it is the sulphur which varies as the numbers 2, 3, 4 and 5. The acid above described is the last term of this class. To the first we have given the name of *sulphuric* series; it contains the acids formerly known; and that of the *thionic* series to the four acids recently discovered. We have thus—

Dithionic..... $S^2 O^5$, hyposulphuric acid of Gay-Lussac and Welter.

Trithionic .... $S^3 O^5$, sulphyposulphuric acid of M. Langlois.

Tetrathionic.... $S^4 O^5$, bisulphated hyposulphuric acid, discovered by us in 1842.

Pentathionic .. $S^5 O^5$, acid under consideration.

This mode of classing the acids of sulphur is conformable to the wants of science, and allows of our adopting the names which have been given to several of these acids by Berzelius.

Pentathionic acid in a free state has the greatest resemblance to the other acids of the series; its solution is not rendered turbid by acids, it does not absorb iodine, and it forms soluble salts with the oxides of the alkalies and the earths. These three characters do not admit of confounding pentathionic acid with hyposulphurous acid.

We have examined it chiefly in its combination with baryta, which may be obtained combined with 1 equiv. of alcohol or with 2 equivs. of water; its formula in the state of hydrate is therefore $S^5 O^5$, BaO + 2HO; it is not very permanent; the alcoholate is more stable. The spontaneous decomposition of the pentathionate of baryta is highly remarkable; by parting with sulphur it may become successively tetrathionate and then trithionate. Sometimes the deposit of sulphur is mixed with sulphate of baryta, and then the liquid has the odour of sulphurous acid. These products, which are formed in greater quantity the higher the temperature, result from the ultimate decomposition of the trithionate:—

$$S^3 O^5, BaO = SO^3, BaO + SO^2 + S.$$

Comptes Rendus, Nov. 2, 1847.

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